THE UNIVERSITY OF ALBERTA


AN EXPERIMENTAL AND SIMULATION STUDY OF THE DEPLETION OF

RETROGRADE HYDROCARBON MIXTURES FROM POROUS MEDIA


By

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

IN PETROLEUM ENGINEERING


DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING


EDMONTON, ALBERTA

FALL, 1972

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies and Research,
for acceptance, a thesis entitled AN EXPERIMENTAL AND SIM-
ULATION STUDY OF THE DEPLETION OF RETROGRADE HYDROCARBON
MIXTURES FROM POROUS MEDIA submitted by Ross Allan Purvis
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy.

# ABSTRACT

The efficient recovery of hydrocarbons from reservoirs which exhibit retrograde behavior is a matter of great commercial importance. There has been some concern and controversy about the effects porous media have on phase behavior in these reservoirs. An apparatus was constructed to study some of the effects porous media have on phase behavior and fluid recovery in retrograde systems. The apparatus could be used for a variety of experiments, however, the experimental work was concentrated on photographing the condensation and vaporization of retrograde liquids from binary mixtures in packs of uniform spheres. It was found that phase equilibrium was always maintained while liquids were condensing, but that it was very difficult to assure equilibrium during vaporization. The tendency for non-equilibrium during vaporization was traced to the nature of the changes in coexisiting phase fugacities with composition.

A computer program was written to simulate the depletion performance of binary and ternary retrograde hydrocarbon mixtures. The vapor-liquid equilibria calculations were based on the Chao-Seader correlation. An interpolation procedure was developed to extend the pressure range of the Chao-Seader correlation to the convergence pressure of the mixture. The phase density calculations were based on equation of state approximations which were developed for some well-known corresponding states correlations.

# ACKNOWLEDGEMENT

The author wishes to express his gratitude and appreciation to the following persons and organizations:

Professor P. M. Dranchuk -- for serving as thesis supervisor;

Professors D. B. Robinson, A. E. Mather, D. L. Flock and C. M. Rodkiewicz -- for serving on the thesis committee and for numerous beneficial discussions;

The machine shop and DACS center personnel of the Department of Chemical and Petroleum Engineering -- for their assistance and co-operation;

Fellow graduate students -- for their discussions with regard to this work;

The National Research Council of Canada, the Petroleum Recovery Research Institute of Calgary and the Aid to Education Fund -- for their financial support of this work;

His wife -- for her understanding and for typing the manuscript;

His family -- for their patience.

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Chapter 1.   INTRODUCTION

## 1.1   Terminology for Retrograde Systems

The adjective "retrograde" is used to designate a direction or a condition which is contrary to a previous direction or an earlier condition.  Katz and Kurata[1] reported that the first use  of retrograde in connection with phase behavior was by Kuenen at Leiden in 1892.  Kuenen used the term "retrograde condensation" to describe the appearance and subsequent disappearance of a liquid phase during isothermal compression of binary mixtures at temperatures above their critical.  Katz and Kurata have given some rules for nomenclature which are now generally used to describe retrograde phenomena in phase behavior.  Their rules are:

1.  Condensation is interpreted as the formation of a more dense or liquid phase, and vaporization is interpreted as the formation of a less dense or vapor phase when the system is on or within the border curve for the two phase system.

2.  The term "retrograde" is used to earmark phase changes in which the direction of temperature or pressure travel causing the phase change is backward from that which causes the phase change for normal cases, such as pure substances or mixtures at low pressure.

3.  Only isothermal or isobaric changes are considered retrograde, since a change in phase accompanying a combined variation of pressure and temperature has no standard of comparison.

4.  If two liquid phases form during an isothermal or isobaric process, then the word "double" will prefix the name

such as double isobaric retrograde condensation.

Figure 1-1 is a schematic phase diagram for a multicompo-
nent hydrocarbon mixture which illustrates the preferred no-
menclature to describe retrograde behavior.  It should be
noted that the term "revaporization" is not required under
these rules.  The border curve in Figure 1-1 is such that both
the bubble point and dew point lines reverse slope to join at
the critical point.  Hence, retrograde condensation can occur
between dew points such as points D and D', and is sometimes
called condensation of the first kind.  Similarily retrograde
condensation can occur between bubble points which is some-
times referred to as condensation of the second kind.  In some
mixtures only the bubble point line or the dew point line
reverses to the critical point, and just one retrograde region
occurs.

In oil-field terminology underground accumulations of
hydrocarbons are broadly classified as gas or oil reservoirs.
Gas reservoirs are multicomponent mixtures which exist in the
gaseous state under initial reservoir pressure and temperature
and can be further classified as:  (a) gas-condensate or ret-
rograde gas, (b) wet gas, and (c) dry gas.

## 1.2  Characteristics of Naturally Occuring Systems

To be classified as a retrograde gas, the reservoir temp-
erature must lie between the critical and cricondentherm
points of the phase diagram for the original mixture.  Since
the reservoir production process occurs at essentially con-
stant temperature, only isothermal retrograde condensation or
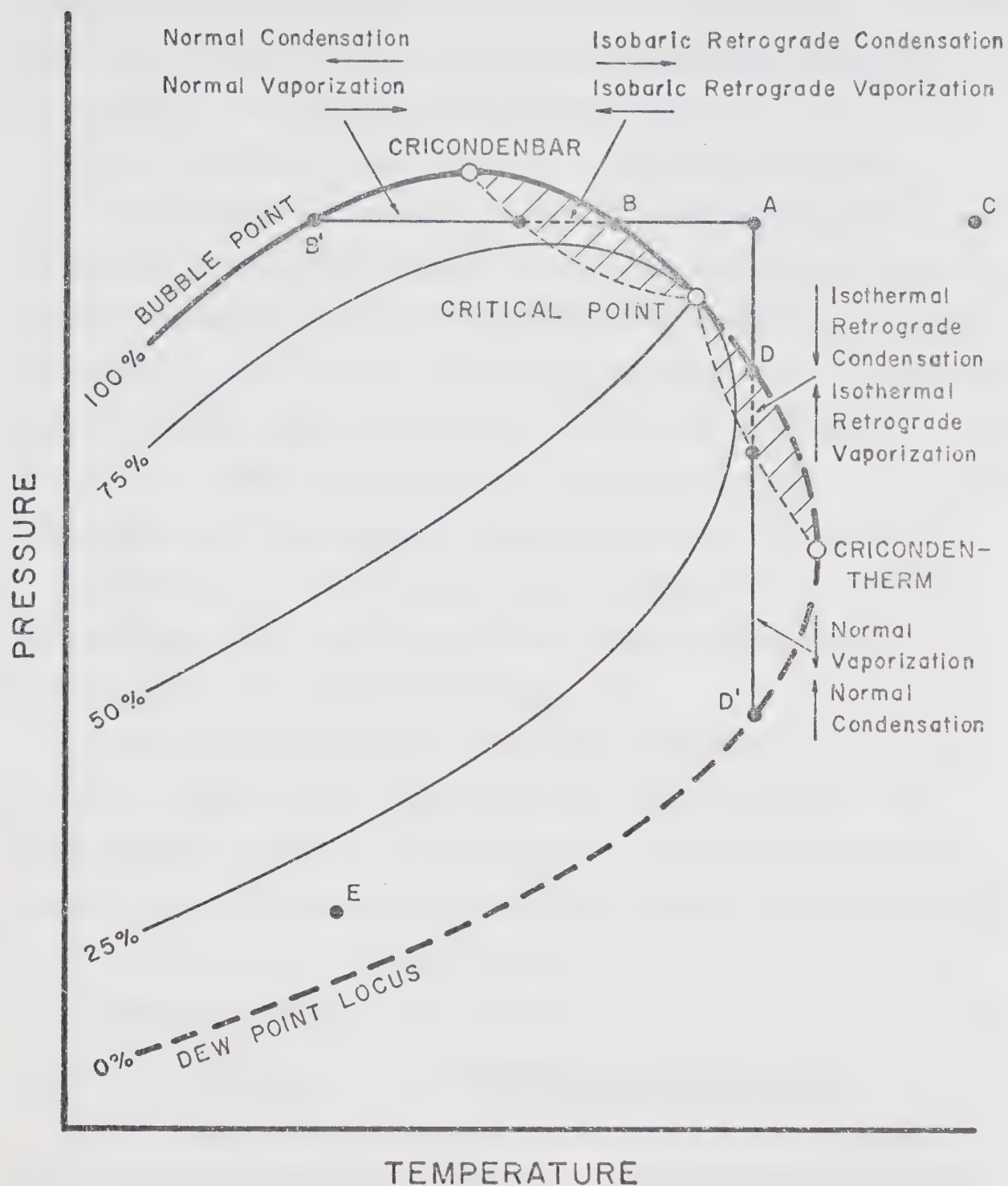
Figure 1-1. Schematic Phase Diagram Illustrating Nomenclature for Retrograde Systems.

vaporization are of interest to reservoir engineers. A reservoir temperature and initial reservoir pressure corresponding to point A of Figure 1-1, and pressure decline along the path A-D' are typical of a gas-condensate or retrograde gas.

Wet gas reservoirs have reservoir temperatures which are in excess of the cricondentherm, and therefore always remain in the single phase gaseous region in the reservoir. Point C of Figure 1-1 is typical of the initial conditions of pressure and temperature for such systems. The term "wet" results from the fact that the system is in the two phase region at surface separator conditions such as those of point E in Figure 1-1. The separator liquid from a wet gas contains fewer heavy hydrocarbons than a retrograde gas, and the quantity of separator liquid recovered is usually less.

Dry gas reservoirs are comprised principally of methane with only minor amounts of intermediate hydrocarbons. No hydrocarbon liquids condense from these mixtures, either in the reservoir or surface facilities. However, water vapor is usually removed to prevent formation of gas hydrates in gas pipelines and distribution systems.

## 1.3  Recovery Methods for Retrograde Gas Reservoirs

The exploitation schemes for wet gas or dry gas reservoirs are much different than those for retrograde gas reservoirs. In the former, a decline in reservoir pressure with continued gas production does not result in the formation of a liquid phase within the reservoir. Therefore, the composition of the produced gas and remaining reservoir gas never

changes. In retrograde gas reservoirs the formation of a reservoir liquid which is rich in the heavier components causes the produced gas and remaining reservoir vapor-liquid mixture to have continuously changing compositions. As the two phase mixture in the reservoir becomes richer in the heavier components, the critical point, and the entire pressure-temperature phase diagram shifts to the right (higher temperature region). This results in a reduced dew point pressure at reservoir temperature which may not be reached at the abandonment pressure. Thus, some of the retrograde liquid is not vaporized, but remains in the reservoir at abandonment.

At the present time there are three general procedures for recovering gas-condensate fluids from constant volume reservoirs (reservoirs in which there is no water influx or other change in reservoir volume). The first and simplest is to produce and market all production after it has been processed into pipeline or residue gas, liquified petroleum gas (LPG), and stabilized condensate. This depletion procedure is characterized by: (a) minimum initial capital investment, (b) high initial cash flow, (c) low recovery of retrograde liquids, and (d) numerous operating problems in the later stages of depletion due to low deliverability and liquid accumulations in producing wells. This method is currently practiced only when the initial retrograde gas is lean, or when the reservoir is too small to justify the expense of an enhanced recovery method.

A second method which was originally investigated by Standing, Lindblad, and Parsons[2] is to initially produce the

reservoir as in the first method, but to initiate residue gas cycling after partial depletion. There are several advantages to this method: (a) minimum initial capital investment, (b) high initial cash flow, (c) good retrograde liquid recovery, (d) deferred capital investment for a compressor plant, (e) compressor plant construction costs are reduced as the design pressure is much less than the original reservoir pressure, and (f) there are fewer operating problems during the later stages of depletion.

The third and most common method of recovery is to initiate residue gas cycling at the start of production, and to continue cycling until the fluid from producing wells becomes largely diluted with injected residue gas. If full pressure maintenance is to be attained makeup gas must be purchased or otherwise be available, since some gas is used for compressor fuel, and the LPG and condensate are sold. The advantages of this method are: (a) the reservoir process is a miscible gas-gas displacement, (b) there is complete recovery of natural gas liquids from that portion of the reservoir swept by dry gas, (c) flow capacity is sustained since a minimum of retrograde condensation occurs in the reservoir, and (d) there are few operational problems during the "blow down" after cycling is stopped. The disadvantages are: (a) large initial capital investment in cycling facilities, (b) higher operating costs, (c) long project life, and (d) deferred gas sales. Some of these disadvantages can be offset by a recently investigated[3] variation which permits gradually declining reservoir pressure by cycling only part of the residue gas.

## 1.4  Literature Review of Experiments to Simulate Retrograde Reservoir Processes

The isothermal retrograde condensation and vaporization processes which occur during the depletion of a reservoir are approximated in commercial laboratories by stepwise differential depletions.  A reservoir sample is charged to a PVT cell and the system is brought to reservoir temperature and original pressure.  A portion of the equilibrium vapor is then removed from the top of the cell, the system equilibrated, and measurements of pressure, liquid volume, and phase composition are made.  The procedure is repeated to some arbitrary lower pressure.  The PVT cells used for these density and vapor-liquid equilibria measurements do not contain a porous medium. Thus there has been some concern as to whether the results of experiments in unpacked cells are representative of the actual behavior in the interstices of the reservoir rock.  There are three major differences between experimental and actual reservoir conditions which have caused concern.

## 1.4  (a) Effect of Porous Media

The effect of a porous medium on the geometry of the vapor-liquid interface is neglected.  The first experimental work with retrograde fluids in the presence of a porous medium was reported in 1948 by Weinaug and Cordell[4].  They depleted binary mixtures of methane-butane and methane-pentane from unconsolidated Ottawa sand packs without a connate water saturation.  The results were compared to the depletion of methane-butane mixtures from an unpacked cell over similar time periods.  This comparison indicated that vaporization of retrograde liquids was aided by the presence of the sand.  The

improved vaporization from the sand was probably a result of increased interfacial area rather than being related to the curved vapor-liquid interface. Oxford and Huntington[5] performed a series of depletion and constant pressure vaporization experiments with nitrogen-hexane, nitrogen-heptane, and a nitrogen-natural condensate mixture in unconsolidated Wilcox sand packs. They concluded that condensates could be vaporized from sands, and that depletion rate, connate water or initial hydrocarbon liquid saturation have a negligible effect on the performance. These conclusions are largely qualitative since the mixtures studied did not exhibit retrograde behavior under experimental conditions, but simply the solubility of hydrocarbons in nitrogen.

The next phase behavior work in a porous medium involved bubble point measurements in crude oil systems. Gimatudinov and Shedlovsky[6] devised a sensitive technique for determining bubble points within cores from a break in the pressure-volume curve. The technique used formation water as an intermediate fluid, and gas pressure rather than piston movement to effect a change in volume and pressure. They found bubble points to be 4 to 5 atm. higher in natural sandstone cores (permeabilities ranged from 0.1 to 2.0 darcies) than the corresponding bubble points (30 to 70 atm.) in unpacked cells. Tindy and Raynal[7] reported similar increases in bubble point pressures for crude oils in unconsolidated packs of sand, glass beads, powdered steel and pumice. They observed that for porous media composed of glass beads with grain diameter varying from 145 microns to 5 mm., that the increase in saturation pressure

was insensitive to grain diameter. They also noted that the chemical nature of the porous medium did not have a marked effect on the magnitude of the increase in saturation pressure.

Two Russian papers[8, 9] reported a method for determining the initial condensation pressure (upper dew point) for retrograde gases in unconsolidated sand packs under flowing conditions. A change in apparent permeability with pressure was observed. The pressure corresponding to the maximum permeability, on a pressure versus permeability diagram, was taken to be the dew point. These pressures were from 8 to 15 atm. higher than the corresponding dew points (206 to 255 atm.) under static conditions in an unpacked cell. Dissertation work by Mamedov[10] also indicated higher upper dew point pressures for gas-condensate mixtures in a porous medium.

A new apparatus[11] for comparing the behavior of retrograde gas mixtures in packed and unpacked cells was reported in 1965, and has been used in several Russian studies of condensate recovery. Trebin and Zadora[12] depleted retrograde gas mixtures from an unpacked cell and from packed cells having specific surface areas of 563, 1307 and 3415 cm.$^2$/cm.$^3$ They tried various depletion rates and found that 4 kg./cm.$^2$/hr. resulted in equilibrium between phases. Their data indicated that: (a) the gas produced from a packed cell always contained less recoverable condensate than the gas from an unpacked cell, (b) increasing the specific surface of the porous medium caused a decrease in the condensate content of the produced gas and in the total condensate recovered by depletion to atmospheric pressure, (c) the richer the initial retrograde gas

mixture, the greater the effect of the porous medium, and (d) the effect of the porous medium on depletion performance decreases with increased temperature.

Smith and Yarborough[13] reported experiments on vaporization of retrograde liquids from unconsolidated sand packs by dry gas injection at 1500 psi and 100°F. Three runs with the methane-pentane system showed that a retrograde liquid saturation of approximately 6.5 per cent could be vaporized by contacting with 2.5 pore volumes of methane. Pentane recovery was found to be independent of sand wettability and connate water saturation. A vaporization run with 7.2 per cent retrograde liquid saturation from a simulated sour gas-condensate (pentane and heptane were used for heavy components) was performed in a sand pack without a connate water saturation. The injected dry gas was a methane-hydrogen sulfide mixture. The pentane was completely recovered by injecting four pore volumes of dry gas, however, six pore volumes of dry gas were required to vaporize all the heptane. It was concluded that retrograde liquids could be completely recovered if they were contacted with sufficient dry gas. A Russian paper[14] reported experiments with a particular gas-condensate mixture at 20°C where no vaporization of the retrograde liquid occured within a packed column. A chemical analysis of the mixture was not reported, so it can only be assumed that the mixture consisted of high boiling point hydrocarbons with very few intermediates. Standing, Lindblad and Parsons[2] reported some calculations to estimate the quantity of dry gas required to vaporize a retrograde

liquid from a reservoir fluid. They stated that laboratory tests were performed to confirm calculations that a retrograde liquid saturation of 7.8 per cent could be vaporized by three pore volumes of dry injection gas at 1310 psia and 195°F.

Other papers in the Russian literature[15, 16] show that effects on phase behavior similar to those for a porous medium can be obtained by adding an inert gas such as helium to the initial mixture to be tested. The helium helps to maintain equilibrium between phases during depletion and increases the dew and bubble point pressures.

Clark[17] showed that the volumetric behavior of pure substances (methane, ethane and propane) are significantly affected by adsorption on sand-clay mixtures when the temperature was below the critical temperature of the substance. However, he noted little if any adsorption when a connate water was present.

Although there is a significant amount of work showing that phase behavior is affected by the presence of a porous medium, the reasons for the effects are largely unknown. Anomalies are usually attributed to curvature of the vapor-liquid interface, and qualitatively explained in terms of capillary, adsorption or other physicochemical phenomena.

1.4 (b) Two-Phase Flow Considerations

The reservoir depletion process is simulated in un-packed cells by repeated withdrawals of a portion of the vapor phase. Thus, it is assumed that the retrograde liquid deposited in the porous medium is immobile. This assumption is valid provided that the total liquid saturation (connate

water plus retrograde liquid) never exceeds the minimum liquid flow saturation (MLFS) required to initiate liquid flow. Ham and Eilerts[18] developed a special core holder which was used in experiments to show that the MLFS is a function of the porous medium, flowing fluids, pressure and flow velocity. In their experiments with a nitrogen-natural condensate fluid, the MLFS varied from 22 to 36 per cent for a sandstone core, and from 8 to 11 per cent for a limestone core. Éfros[19] studied the effect liberation of solution gas had on gas and liquid relative permeabilities. He presented a two-parameter permeability relationship which was a function of saturation, pressure gradient and gas-liquid viscosity ratio.

The maximum retrograde liquid volumes for naturally occurring systems seldom exceed ten per cent, so the assumption that retrograde liquids are immobile is usually valid for the bulk of the reservoir. The logarithmic nature of pressure profiles for radial flow causes retrograde liquids to condense and accumulate near the well bore. Thus, a region of two-phase flow often develops around producing wells. Hurst, Goodson and Leeser[20] have shown that deliverablility can be seriously affected by these liquid accumulations.

## 1.4  (c) Effect of Connate Water

Formation water is not present in unpacked cells, but is always present in reservoir rocks. Water is left out of commercial PVT studies because it complicates analyses and can result in severe corrosion if the mixture contains acid gases. The chief concern with water centers around the solubility of reservoir fluids in it. The paraffin hydrocarbons are very

slightly soluble in water, however, carbon dioxide[21] and hydrogen sulfide[22] are moderately soluble, and their release from connate water with declining pressure may cause a considerable difference in composition between experimental and reservoir conditions.

It is also known that in binary hydrocarbon-water systems the critical point between gas and hydrocarbon rich liquid occurs at a higher pressure[23] than the critical pressure for the pure hydrocarbon. Assuming the critical pressure of a multicomponent mixture is also higher, one would also expect the bubble and dew point pressures to be higher. This may account for the anomalous increase in bubble and dew point pressures in the presence of a porous medium having a connate water saturation.

Another factor to be considered is that most reservoir rocks are water wet. Thus water will occupy the smallest pore spaces. This has the effect of decreasing the adsorption of gas-condensate fluids[24, 25]. Connate water also reduces the quantity of retrograde liquid required to exceed the MLFS.

## 1.5 Objectives and Procedures

The purpose of this work was twofold. The first objective was to devise and conduct some experiments which would answer some of the questions concerning the effects of porous media on retrograde behavior that were discussed previously. This work was concentrated on experiments to study the effects of curvature on vapor-liquid equilibria of well defined binary hydrocarbon systems. Identical samples were depleted from

packed and unpacked cells and the results compared. Bubble or
dew point pressures were also measured in packed and unpacked
cells. Photographs were taken of the retrograde liquid capil-
lary structures which formed during the depletion of a binary
mixture from a pack of uniform spheres. A theoretical analysis
of the liquid structures may be found in another report[26].

The second objective was to develop a computer phase
behavior routine capable of simulating the depletion perform-
ance of high-pressure retrograde systems. The vapor-liquid
equilibria portion of the computer progam used a combination
of several well-known methods. The Chao and Seader[27] corre-
lation was used to generate compositionally dependent equilib-
rium ratios which were extrapolated to the system convergence
pressure using an approximating formula proposed by Green and
Hachmuth[28]. The system convergence pressure was determined
in accordance with a definition given by Rowe[29]. The vapor
phase density was calculated from an approximation developed
for the well-known Standing and Katz correlation[30] for natural
gases. The density of the liquid phase was calculated from a
new approximation method which was applied to the correspond-
ing states correlation of Lydersen, Greenkorn and Hougen[31].

Chapter 2.  EXPERIMENTAL APPARATUS AND OPERATING PROCEDURE

## 2.1  General Description of Apparatus

An apparatus was designed and constructed which permitted the phase behavior of a mixture in a PVT cell packed with a porous medium to be directly compared to the phase behavior of the same mixture in an unpacked cell.  This involved the comparison of vapor phase compositions at equal pressures for the packed and unpacked cells.  It also involved the comparison of simultaneous bubble or dew point pressures in packed and unpacked cells.  The same apparatus was used to obtain photographs of liquid structures formed by retrograde liquids in various packs of uniform shperes.

Three 60 ml. windowed cells (Jerguson Model 19T40) were arranged as shown in Figure 2-1.  The cells were mounted on an inner frame suspended by several springs.  The inner frame could be vibrated with an eccentric drive assembly which was rotated with a variable speed electric motor.  Mixing between phases in the two vertical cells was achieved through mercury splashing during vibration.  The cells were enclosed in a constant temperature air bath.  Two large double windows in the air bath allowed full view of the cells and auxilliary fittings. The air bath temperature was maintained with a Hallikainen controller (Model 1253A) connected to a 2 KW heater load, while up to 3 KW of constant heater load could be supplied directly through a separate voltage regulator.  A ten inch fan was used to circulate air within the bath.  This resulted in temperature control within ± 0.1°F at 100°F where most of
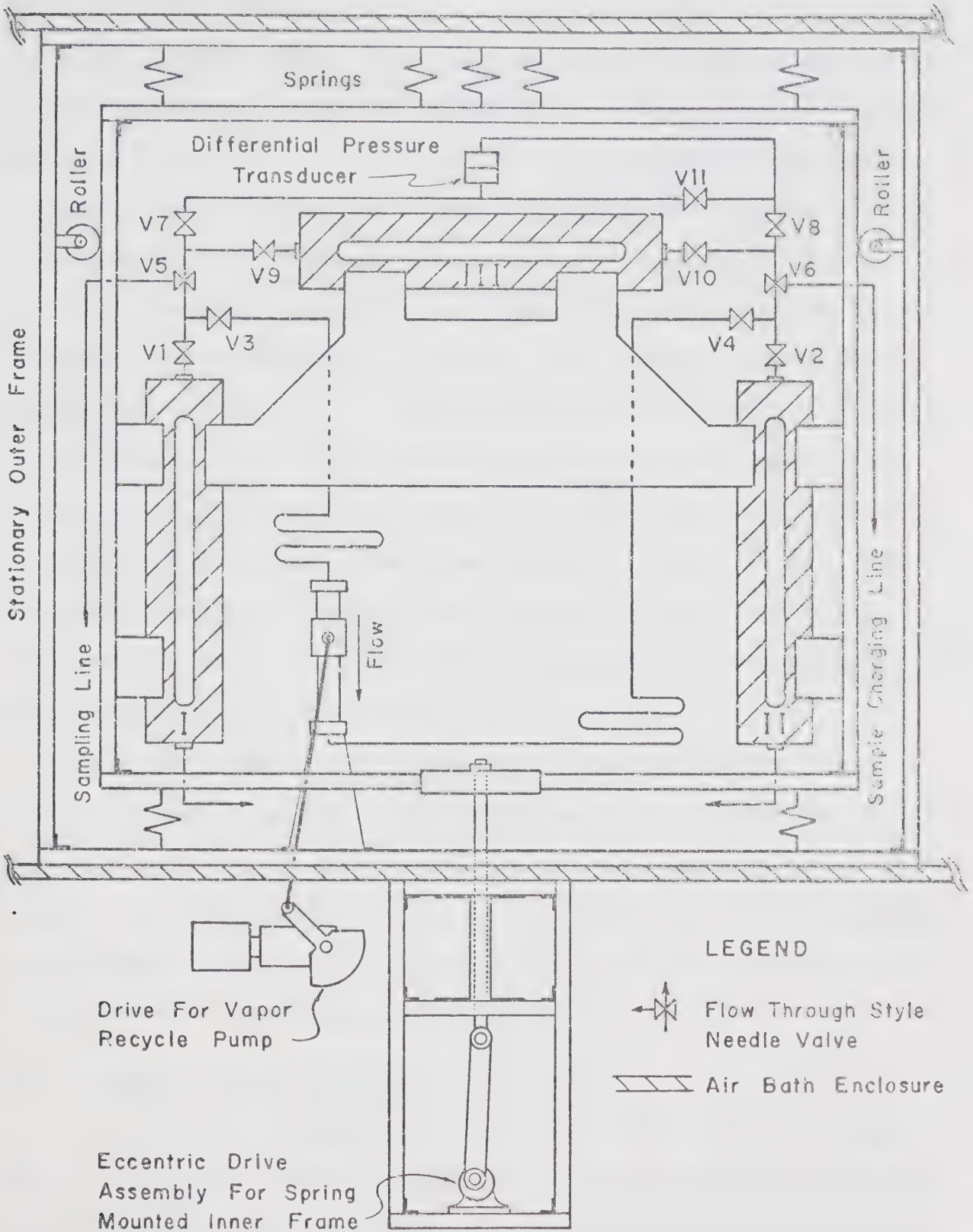
Figure 2-1.  Schematic Diagram of Apparatus for Study of
Retrograde Phenomenon in Porous Media.

the data were taken.

All valves within the air bath were manually operated by reaching through long-sleeve insulated gloves attached to the wall of the bath. By working through the gloves, the bath temperature was not altered while operating valves or taking photographs with a camera mounted inside the air bath.

The mercury volume in each vertical cell could be simultaneously or independently varied with a Ruska proportioning pump (Model 2218 WII). The pressure in the two vertical cells was measured with precision Bourdon tube gauges (Heise, 16 inch dial). Two gauges (0-1500 psi and 0-5000 psi) were connected to the mercury line from each cell, and the dial readings corrected for the variable mercury head in the cells. The temperature in each cell was measured with a thermocouple which protruded into the cell.

The horizontal cell always contained a pack of glass beads or ball bearings. To equilibrate the retrograde liquid in this cell, vapor was circulated with a Ruska vapor recycle pump. The flow through the pump was always in the direction indicated on Figure 2-1 to avoid any possible accumulation of liquids within the pump or lines.

## 2.2 Sampling and Analyses

A schematic diagram of the vacuum system used to transfer vapor phase samples directly to either an electro-magnetic gas density balance or a research chromatograph is shown in Figure 2-2. Vapor samples were admitted to the sample system by opening the micro-needle valve V5. Valve V5 featured a
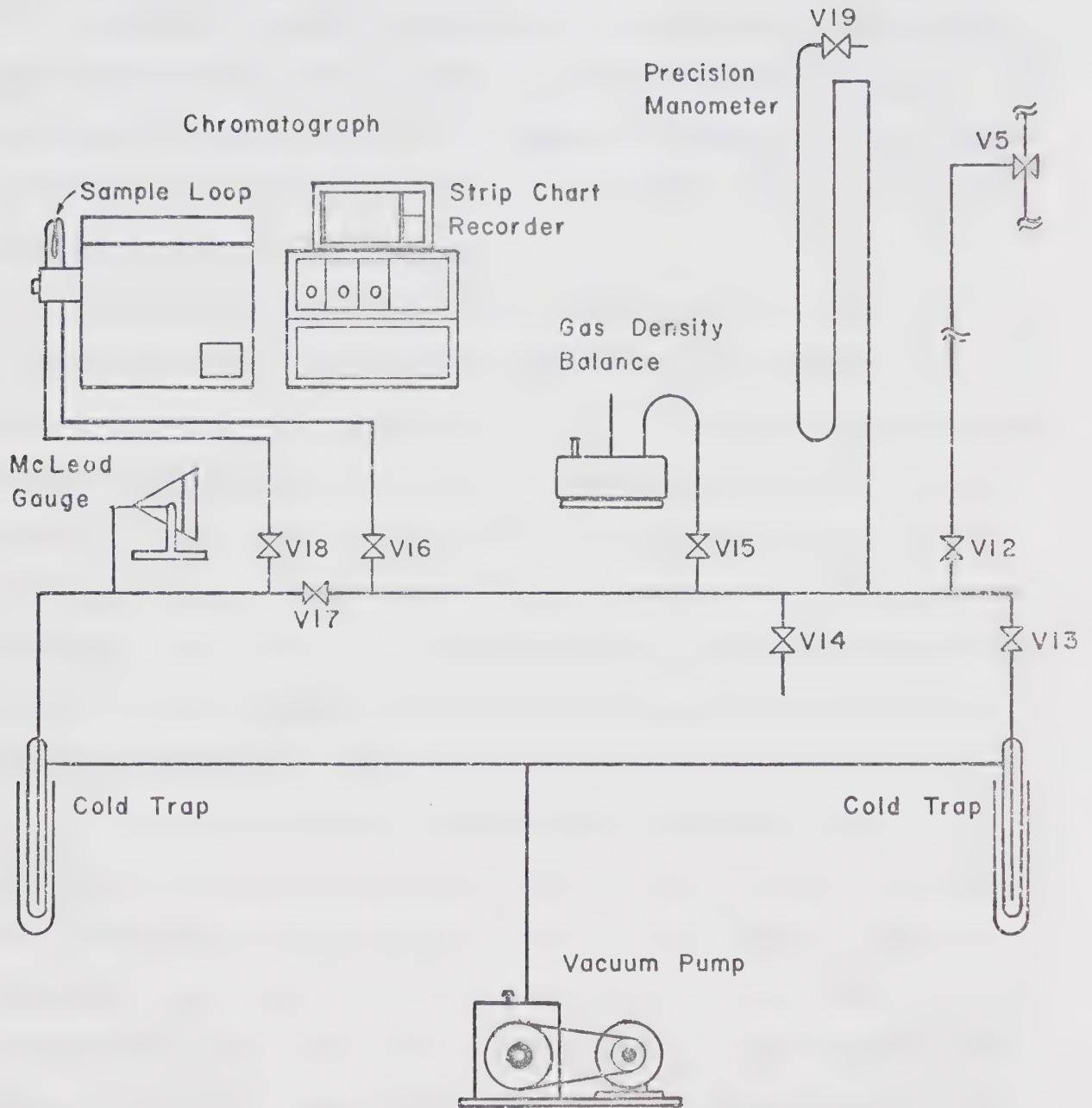
Figure 2-2. Schematic Diagram of Sample Analysis Section

flow-through design which eliminated sampling stagnant vapor from dead-end lines or fittings. The need for external heating to prevent liquid condensation from samples was avoided by keeping the sample system at subatmospheric pressure. The precision manometer gave the absolute pressure in the sample system as the space between valve V19 and the mercury column was kept under a high vacuum.

To prepare the system for a new sample all the valves in Figure 2-2 were opened except valves V5, V14 and V19, and the entire system was evacuated to less than five microns (McLeod gauge reading). If a sample was to be taken for density balance analysis valves V12 and V15 were opened and all other valves closed. Then, valve V5 was opened until the desired pressure was observed on the manometer. Several measurements could be made on the same sample by simply opening valve V13 for an instant to reduce the pressure on the sample system.

If a chromatograph sample was to be taken, valves V12 and V16 were opened and all other valves closed. The sample was admitted through valve V5 until a particular reference pressure was observed on the manometer. Then, valve V16 was closed and the sample was introduced into the chromatograph. After the sample was introduced into the chromatograph the lines connecting the sample loop to valves V16 and V18 became filled with carrier gas (helium). This gas was evacuated through valve V18 without contaminating the remaing sample which could be used for a duplicate analysis.

The micro-metering valve V15 was used to introduce reference gases for calibration of the density balance and

chromatograph.

## 2.3   Loading and Mixing a New Charge

Prior to loading a new charge, all of the valves in Figure 2-1 were opened except V5 and V6.  The entire system was then purged with methane and vented to atmospheric pressure.  Next, the least volatile component in the mixture (butane, pentane, or hexane) was admitted through valve V6.  Sample valve V5 was opened and closed as required to control the quantity of least volatile component admitted to the system.  If a ternary mixture was being prepared the intermediate component was added next, otherwise methane was added.

Sufficient mercury was pumped into cells I and II to increase the system pressure above the upper dew point of the mixture.  The mixture was then circulated through the packed cell with the vapor recycle pump.  During circulation, the contents of cells I and II were periodically injected, withdrawn, and reinjected into the system to ensure a homogeneous mixture.

After mixing, a sample was taken through valve V5 and the composition of the mixture determined.  If the desired composition was not attained, the mercury level was brought to the top of cell II and valves V4, V8 and V10 closed.  The pressure in cell II was lowered by withdrawing mercury and more of the deficient component added to cell II.  Mercury was again pumped into cell II until the pressure was equal to that in the other cells.  Valves V4, V8 and V10 were then opened and the components mixed as before.  This process was

repeated until the desired composition was attained.

## 2.4  Unpacked Cell Depletion

After mixing, all of the contents of cell II and all but about 15 ml. of the contents of cell I were compressed into cell III and the vapor recycle pump. Then valves V3, V4, V9 and V10 were closed, and valves V1, V2, V7, V8 and V11 left open. This procedure stored a charge having the same initial composition for a subsequent run in which the packed cell was depleted.

The depletion of a constant volume gas-condensate reservoir is a differential process which can be approximated as a series of flash liberations. The series of flashes was performed as follows. Valve V1 was closed, and mercury was withdrawn from cell I while shaking to maintain equilibrium between phases. After the pressure in cell I was lowered to some predetermined value, mercury was withdrawn from cell II until both cells were at equal pressure. Then valve V1 was opened and mercury simultaneously added to cell I and withdrawn from cell II until the mercury level in cell I was restored to its initial level. Valve V1 was closed again and the amount of retrograde liquid in cell I was measured with a cathetometer. A vapor sample was then expanded into the composition analysis section through valve V5. This procedure was repeated until either all the retrograde liquid had vaporized, or the system pressure was depleted to some arbitrary lower limit. Whenever the withdrawals from cell I had nearly filled cell II, valve V8 was closed and the contents of cell

II were vented through valve V6.

## 2.5  Packed Cell Depletion

After depleting the unpacked cell, valves V1, V7 and V8 were closed.  Next, the mercury level in cell II was raised to the top of the cell and the contents vented through valve V6.  Then valves V3, V4, V9 and V10 were opened.  The pressure drop caused by opening these valves was usually about 300 psi so that the charge, previously stored in the packed cell and recycle pump, remained above its dew point.  The vapor recycle pump was then started, and after about an hour of mixing an initial sample was taken.

The differential depletion of the packed cell was performed by slowly withdrawing mercury (2.5 to 15.0 ml./hr.) from cell II.  Vapor samples were taken at regular intervals of pressure, and in some experiments photographs were taken of the liquid capillary structures which formed at the window of the Jerguson cell.  Whenever the mercury level reached the bottom of cell II, valves V4 and V10 were closed and the contents of cell II were vented through valve V6.

## 2.6  Simultaneous Packed Cell and Unpacked Cell Dew or Bubble Point Determination

An initial charge was prepared and sampled as previously described.  Then the system volume was adjusted so that cell I was full of mercury and the space above the mercury in cell II was slightly greater than the pore volume of cell III.  If necessary, part of the charge was bled through valve V6 until the system pressure was about 100 psi above the estimated dew

or bubble point.

Valves V3, V4, V10 and V11 were then closed and the run started by slowly withdrawing mercury from cells I and II at equal rates, typically 2.5 to 10.0 ml./hr. The differential pressure between the unpacked system (cell II) and the other system (consisting of cell I and the packed cell III) was measured by recording the output voltage from a sensitive differential pressure transducer (75 psi span) on a strip chart recorder. A typical chart is shown in Figure 2-3. The differential pressure between the two systems could be esti-mated from the chart within 1 psi. Two event markers on the recorder were used to record every 10 psi pressure drop in the open and packed systems as indicated by the Heise gauges. Since the packed system had a smaller initial cell volume than the unpacked system, and the rate of volume increase was equal for both cells, the bubble or dew point was reached first in the packed cell. The formation of two phases of different density caused a break in the pressure-volume curve traced by the recorder. Later, a similar break resulted from the formation of two phases in the unpacked cell. This dif-ferential technique provided a sensitive method of determin-ing if the presence of a porous medium had any significant effect on the bubble or dew point pressures of the mixtures studied.

## 2.7  Vaporization Of Retrograde Liquid from the Packed Cell

An experiment to model the vaporization of a retrograde liquid from a porous medium by contacting with dry gas at
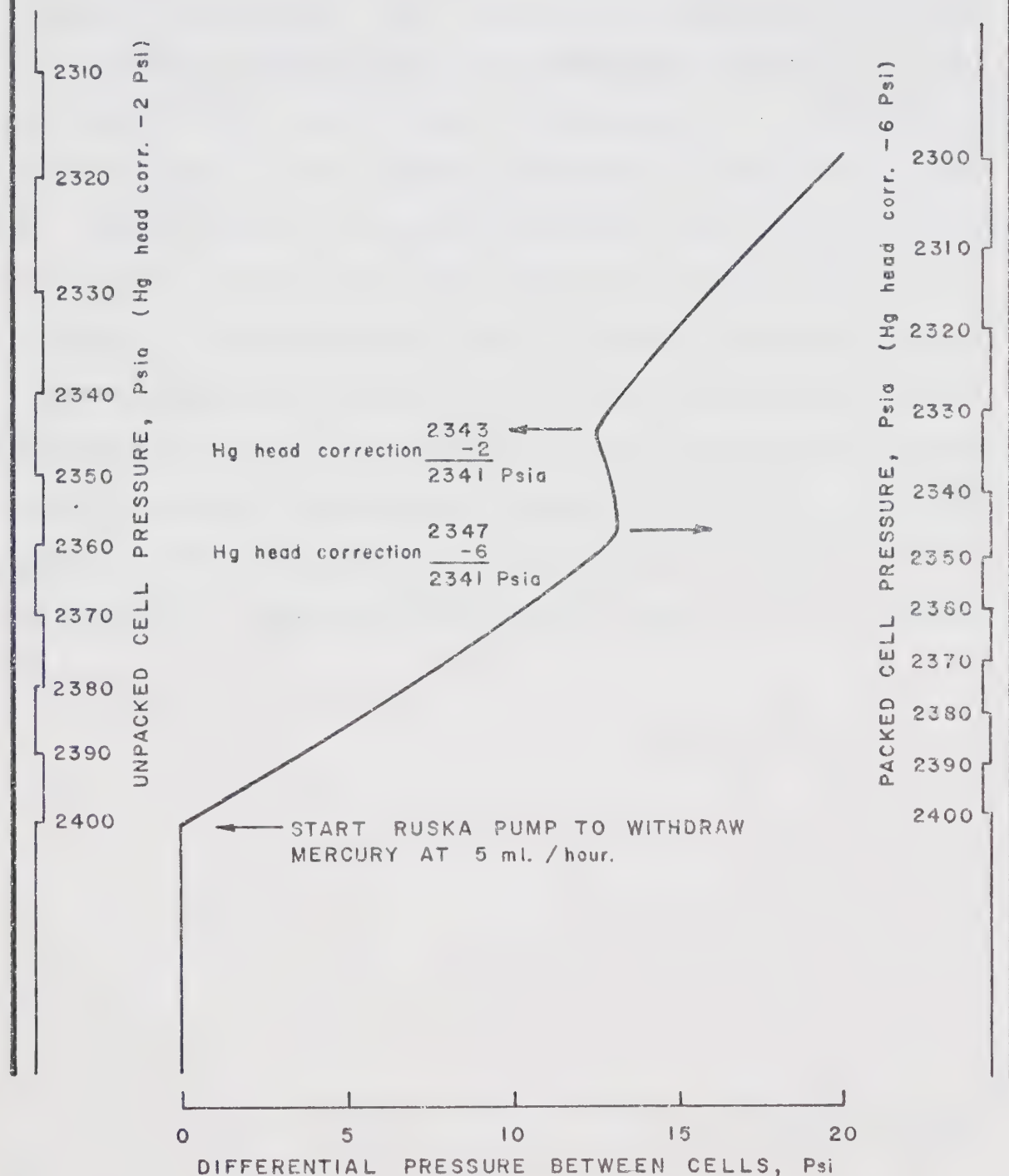
Figure 2-3.  Typical Chart for Dew Point Determinations in
Packed and Unpacked Cells.

constant pressure was performed as follows. An initial charge
was prepared and sampled as previously described. After par-
tially depleting the packed cell, valves V3, V4, V9 and V10
were closed and the contents of cells I and II vented and
purged with methane. Cell II was then filled with methane
at a pressure equal to the final depletion pressure of cell
III, while cell I was filled with mercury. To start the run,
valves V7 and V8 were closed and valves V9 and V10 were open-
ed. Mercury was simultaneously added to cell II and withdrawn
from cell I at the same rate (usually 2.5 or 5.0 ml./hr.).
Samples of produced vapor from the packed cell were taken at
regular intervals. Removal of a sample would cause a small
decrease in system pressure which could be restored by tempo-
rarily stopping the mercury withdrawl from cell I. By using
this procedure the number of pore volumes of dry gas required
to vaporize a particular retrograde liquid could be determin-
ed.

Chapter 3.   EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

## 3.1  Materials

Matheson CP grade methane was used without further puri-
fication on all runs except Run 10.  The manufacturer claims
99.0 per cent minimum purity for CP grade.  Mass spectrometer
and chromatograph analyses also indicated 99.0 per cent purity
with the following impurities:  0.7 mole per cent nitrogen,
0.2 per cent ethane, and 0.1 mole per cent carbon dioxide.

The n-butane used was Matheson instrument grade for which
the manufacturer stated 99.5 per cent minimum purity for the
liquid phase.  A liquid sample was transferred to a stainless
steel cylinder and the sample was repeatedly cooled in a liq-
uid air bath and evacuated to less than five microns (McLeod
gauge) to remove non-condensibles.  Chromatograph analysis of
this liquid sample indicated approximately 0.1 mole per cent
of each of the following:  i-butane, i-pentane and n-pentane.

The n-pentane and n-hexane used were Phillips pure grade
with a minimum stated purity of 99.0 per cent.  Chromatograph
analysis indicated the n-pentane to contain 0.4 mole per cent
i-pentane and 0.2 mole per cent of an isomer of hexane.  A
similar analysis of the n-hexane revealed 0.8 mole per cent
of a higher boiling point isomer of hexane.  The pentane and
hexane were not further purified except to strip any entrap-
ped air prior to loading by slowly bubbling methane through
the loading burette on the charging system.

Run 10 was made with Matheson UHP methane (99.97 per
cent purity) and the middle cut of distilled Phillips pure

grade n-pentane.

The materials used to simulate porous media and other packed cell data are summarized in Table 3-1. These materials were thoroughly washed with acetone prior to packing. After the packed cell was mounted on the apparatus it was flushed with pentane.

## 3.2  Calibrations and Sources of Error

Static pressures were measured with Heise gauges which were found to be linear within 0.1 per cent of full scale when calibrated against a Ruska dead weight tester. Pressures in the range from 40 to 1300 psia could be estimated to within 1 psi after correcting for the variable mercury head in the cells. Pressures in the range from 1300 to 4000 psia are believed to be accurate within 3 psi. Other pressure calibration data are summarized in Appendix H.

The iron-constantan thermocouples in each cell were calibrated in a water bath with a precision mercury thermometer. The calibration data are given in Appendix H. The reference junction and potentiometer used for calibration were also used to take the data. The calibration was believed to be accurate within 0.05°F, however the air bath enclosure could only be controlled to within 0.1°F.

The electro-magnetic gas density balance was calibrated with the following gases:  helium, methane, nitrogen and carbon dioxide. The calibration data in Appendix G indicate the same slope of current versus density for all gases after adjusting the molecular weights for trace impurities. The

TABLE 3-1

SUMMARY OF POROUS MEDIA AND PACKED CELL DATA

30-40 US Mesh Glass Beads:

    Density of glass beads . . . . . .    2.515 gm./cc.

    Weight of beads in the pack . . . .    89.60  gm.

    Volume of beads in the pack . . . .    35.63  ml.

    Valve-to-valve volume of cell . . .    60.30  ml.

    Cell volume packed with beads . . .    56.30  ml.

    Porosity . . . . . . . . . . . . .    36.70  %

3/32 inch Chrom-steel Ball Bearings:

    Density of ball bearings . . . . .    7.716 gm./cc.

    Weight of bearings in the pack . .  268.34  gm.

    Volume of bearings in the pack . .    34.83  ml.

    Valve-to-valve volume of cell . . .    60.9   ml.

    Cell volume packed with bearings .    58.4   ml.

    Porosity . . . . . . . . . . . . .    40.4   %

1 mm. Stainless Steel Ball Bearings:

    Density of ball bearings . . . . .    7.701 gm./cc.

    Weight of bearings in the pack . .  290.57  gm.

    Volume of bearings in the pack . .    37.73  ml.

    Valve-to-valve volume of cell . . .    60.9   ml.

    Cell volume packed with bearings .    58.4   ml.

    Porosity . . . . . . . . . . . . .    35.5   %

vapor phase analyses tabulated in this chapter were all cal-
culated from density measurements. Repeatibility of analyses
was 0.1 mole per cent or better. The largest source of error
in density balance analyses was caused by approximately one
mole per cent of impurities in all runs except Run 10. For
density balance calculations methane and the light impurities
were treated as a pseudo-component with a molecular weight of
16.2. True molecular weights were used for the heavy compo-
nents since their impurities were generally isomers with the
same molecular weight. True molecular weights were used for
Run 10 and good agreement was observed with other runs where
the pseudo-light component molecular weight was used.

## 3.3   Methane and n-Butane Mixtures

Four runs at 100°F were made with the methane and n-butane
system and the results are summarized in Table 3-2. The same
packing material (3/32 inch diameter ball bearings) was used
in all runs. Both packed and unpacked cell depletions were
performed in Runs 4, 5 and 13. Run 14 was a repeat of the
packed cell depletion in Run 13 to resolve the composition
difference between the packed and unpacked cells and to obtain
improved photographs of the retrograde liquid structures.

A comparison of the vapor compositions for the packed
and unpacked cells indicates that equilibrium was not always
maintained during the vaporization portion of the depletions.
This is particularly evident in Run 5 at pressures below 600
psia where the produced vapor compositions differ by as much
as 12 mole per cent. Photographs of liquid structures from

TABLE 3-2

COMPOSITION AND PER CENT LIQUID DATA FOR
METHANE AND N-BUTANE MIXTURES

| Press. Psia | Run 4. 3/32 in. Sphere Pack Temperature 100°F | | | | Run 5. 3/32 in. Sphere Pack Temperature 100°F | | | |
|---|---|---|---|---|---|---|---|---|
| | Mole Frac. $CH_4$ | | Liquid Volume | | Mole Frac. $CH_4$ | | Liquid Volume | |
| | Unpacked Cell | Packed Cell | Meas. % | Calc. % | Unpacked Cell | Packed Cell | Meas. % | Calc. % |
| Initial | 0.864 | 0.864 | 0.0 | 0.0 | 0.816 | 0.815 | 0.0 | 0.0 |
| 1750 | 0.862 | 0.865 | 0.0 | 0.0 | 0.828 | 0.828 | 2.1 | 7.5 |
| 1500 | 0.867 | 0.867 | Trace | 0.91 | 0.868 | 0.865 | 9.7 | 10.0 |
| 1250 | 0.881 | 0.881 | 1.10 | 1.70 | 0.881 | 0.880 | 9.7 | 9.2 |
| 1000 | 0.884 | 0.885 | 0.95 | 1.42 | 0.885 | 0.883 | 8.2 | 7.9 |
| 800 | 0.881 | 0.881 | 0.95 | 1.01 | 0.880 | 0.882 | 6.8 | 6.9 |
| 600 | 0.863 | 0.866 | 0.47 | 0.41 | 0.865 | 0.874 | 6.0 | 5.8 |
| 400 | 0.840 | 0.854 | 0.0 | 0.0 | 0.828 | 0.857 | 3.7 | 4.5 |
| 200 | 0.835 | 0.859 | | | 0.708 | 0.747 | 1.0 | 2.0 |
| 150 | | | | | 0.637 | 0.758 | 0.6 | 1.2 |
| 100 | | | | | 0.607 | 0.671 | 0.0 | 0.0 |

| Press. Psia | Run 13. 3/32 in. Sphere Pack Temperature 100°F | | | | Run 14. 3/32 in. Sphere Pack Temperature 100°F | | | |
|---|---|---|---|---|---|---|---|---|
| | Mole Frac. $CH_4$ | | Liquid Volume | | Mole Frac. $CH_4$ | | Liquid Volume | |
| | Unpacked Cell | Packed Cell | Meas. % | Calc. % | Unpacked Cell | Packed Cell | Meas. % | Calc. % |
| Initial | 0.849 | 0.858 | 0.0 | 0.0 | | 0.855 | | 0.0 |
| 1500 | 0.868 | 0.865 | 0.32 | 3.39 | | 0.863 | | |
| 1250 | 0.882 | 0.881 | 1.77 | 3.74 | | 0.881 | | |
| 1000 | 0.884 | 0.883 | 1.45 | 3.19 | | 0.885 | | |
| 800 | 0.881 | 0.880 | 0.97 | 2.62 | | 0.880 | | |
| 600 | 0.865 | 0.866 | 0.32 | 1.89 | | 0.868 | | |
| 400 | 0.829 | 0.829 | Trace | 0.83 | | 0.836 | | |
| 300 | | 0.800 | | | | 0.798 | | |
| 200 | 0.803 | 0.800 | | 0.0 | | 0.798 | | |

Run 5 indicated liquid rings of varying sizes with gravity segregation (liquid accumulation along the bottom of the horizontal cell). The two prime factors contributing to non-equilibrium were that the depletion rate was too rapid and the sphere size too large. Although the depletion rate was comparable to that in the other runs, the liquid saturation (equilibrium data predict a maximum saturation of 9 per cent) was from three to six times greater. The large sphere size could not support all the liquid and gravity segregation resulted causing reduced interfacial area for mass transfer.

The composition isotherms for equilibrium phases in binary mixtures are fixed, and experimental results can be directly compared with other published data. Figure 3-1 makes this comparison for vapor phase compositions and good agreement with the data of Sage, Hicks and Lacey[32] is observed. The data of Weinaug and Cordell[4] were obtained by depleting a retrograde mixture from an Ottawa sand pack in nine hours. The short vertical lines give the average composition of a vapor sample removed during the indicated pressure drop.

The calculated compositions shown on Figure 3-1 were obtained from equilibrium flash calculations and are discussed further in Chapter 6.

Two values are reported in Table 3-2 for the liquid volume. The "measured per cent" column gives the percentage of retrograde liquid observed in the unpacked call by sighting with a cathetometer. This measurement was not very precise for liquid saturations less than about 10 per cent. It was
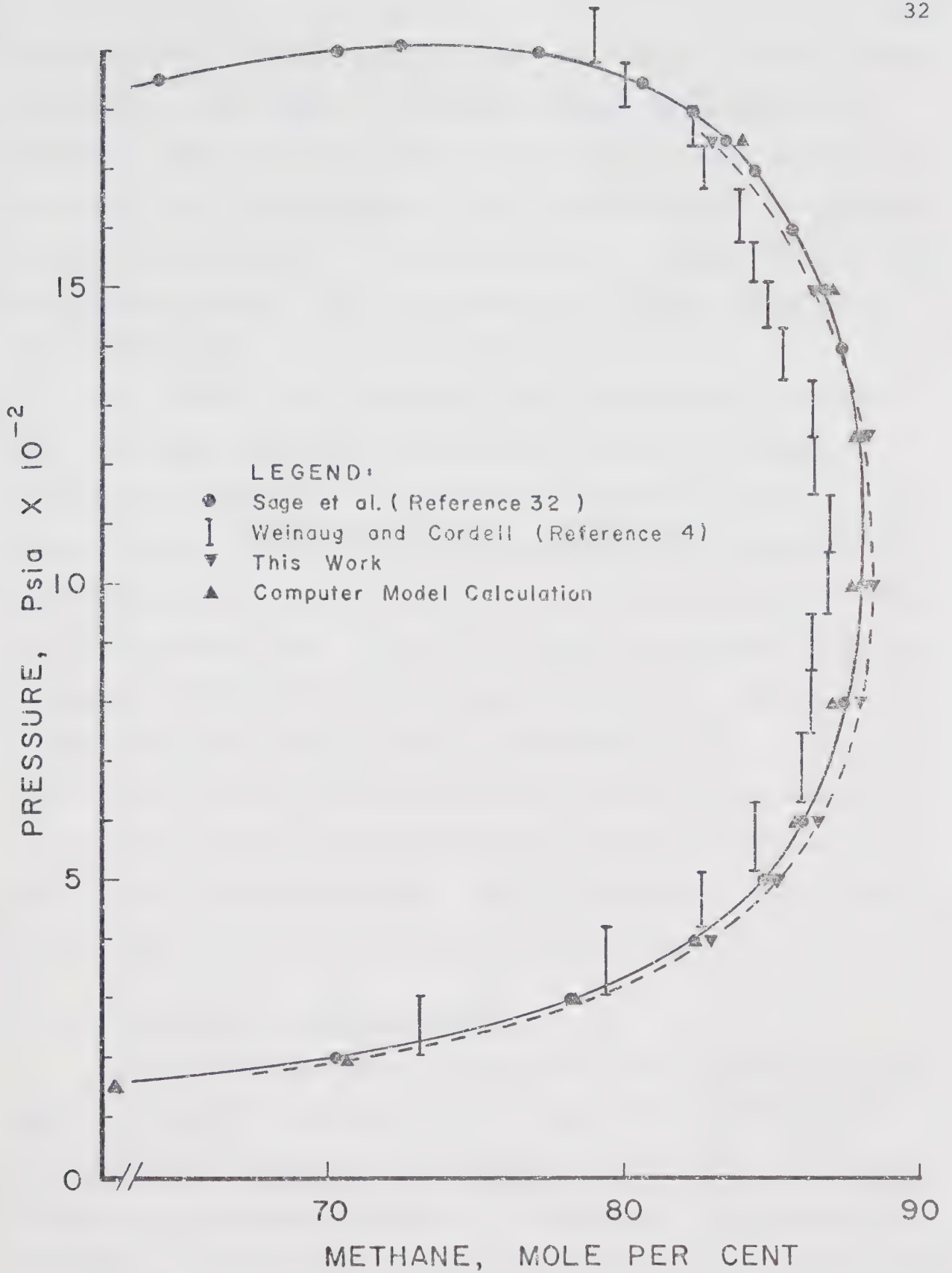
Figure 3-1. Pressure-Composition Isotherms for the Methane and n-Butane System at 100°F.

very difficult to distinguish the true meniscus, and it would take up to three hours for all the liquid to settle after shaking. Readings were taken a few minutes after shaking was stopped. The "calculated per cent" column gives the per cent liquid from a series of flash calculations which modelled the depletion process in the unpacked cell. These calculations and results are discussed in Chapter 6.

The packed cell depletions were differential processes. For retrograde systems a differential depletion results in less liquid than that obtained from a series of flash liberations. Thus, the equilibrium retrograde liquid saturations in the packed cell would be smaller than the observed saturations in the unpacked cell. Figure 3-2 shows retrograde liquid saturations for a differential depletion process. The two-phase equilibrium and density data of reference 32 were used to prepare this figure. It should be noted that large changes in liquid saturations result from minor changes in the composition of the initial mixture. This figure may be used to estimate the liquid saturations in the packed cell.

## 3.4 Methane and n-Pentane Mixtures

Eight runs were made with methane and n-pentane mixtures and the results are summarized in Table 3-3. Runs 1 and 2 were shakedown runs, and the temperature was less than 100°F because the reference junction was not used in an early thermocouple calibration. Attempts to photograph the liquid structures in these two runs were unsuccessful because of multiple reflections of the flood lamps on the glass beads. The
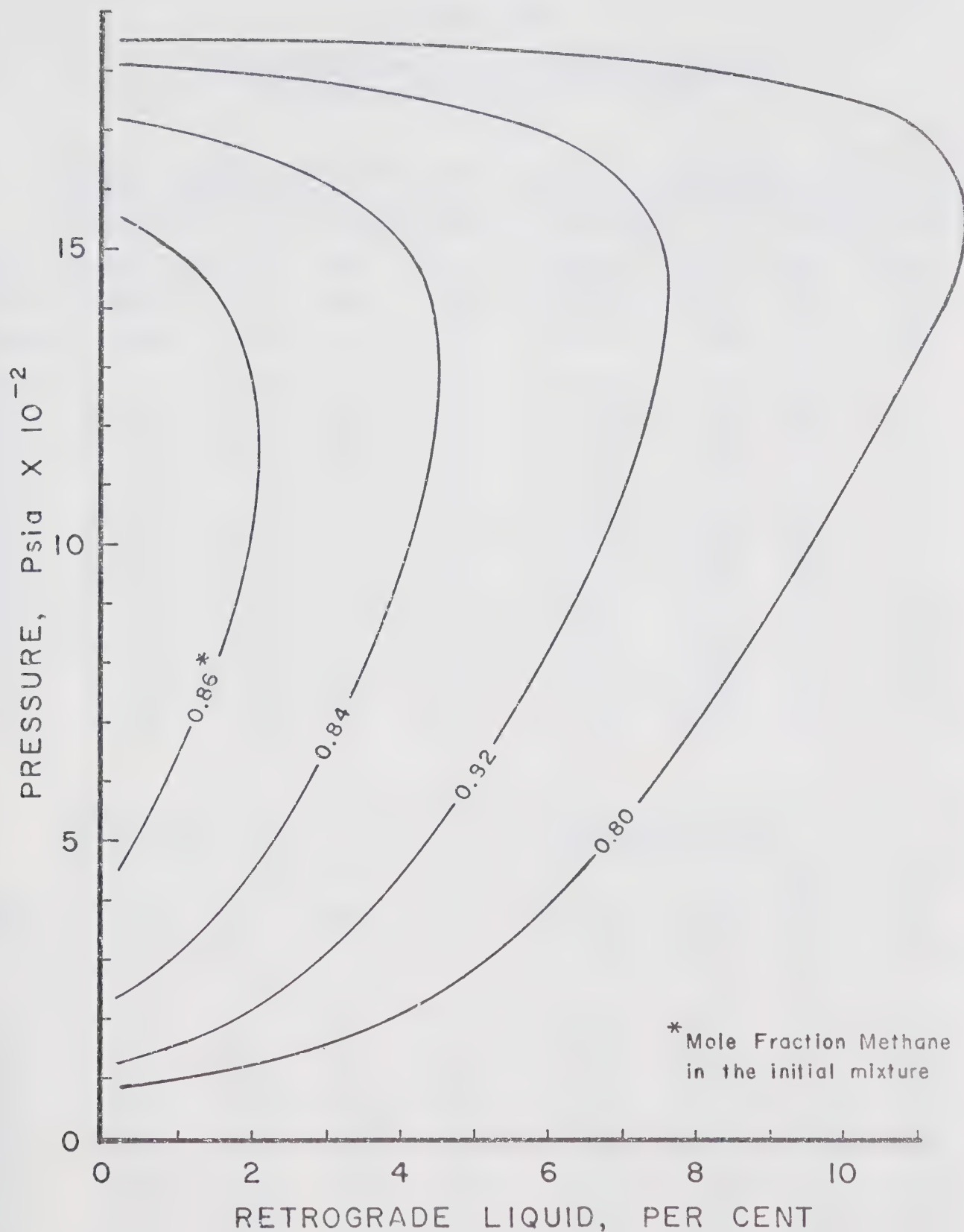
Figure 3-2.   Retrograde Liquid Saturation for Differential
              Depletion of Methane-n-Butane Mixtures.

TABLE 3-3

COMPOSITION AND PER CENT LIQUID DATA FOR
METHANE AND N-PENTANE MIXTURES

| | Run 1. 30-40 U.S. Mesh Glass Beads, Temperature 99.5°F | | | | Run 2. 30-40 U.S. Mesh Glass Beads, Temperature 99.7°F | | | |
|---|---|---|---|---|---|---|---|---|
| | Mole Frac. $CH_4$ | | Liquid Volume | | Mole Frac. $CH_4$ | | Liquid Volume | |
| Press. Psia | Unpack- ed Cell | Packed Cell | Meas. % | Calc. % | Unpack- ed Cell | Packed Cell | Meas. % | Calc. % |
| Initial | 0.881 | 0.882 | 0.0 | 0.0 | 0.911 | 0.912 | 0.0 | 0.0 |
| 2250 | 0.911 | 0.910 | 4.8 | 10.8 | 0.911 | 0.911 | 0.0 | |
| 2000 | 0.934 | 0.934 | 13.1 | 11.6 | 0.936 | 0.939 | 4.4 | 3.7 |
| 1750 | 0.947 | 0.950 | 13.5 | 11.6 | 0.949 | 0.953 | 6.5 | 5.2 |
| 1500 | 0.956 | 0.958 | 13.7 | 10.7 | 0.954 | 0.959 | 7.1 | 5.1 |
| 1250 | 0.960 | 0.949 | 13.9 | 9.9 | 0.964 | 0.965 | 6.8 | 4.9 |
| 1000 | 0.964 | 0.964 | 13.5 | 9.1 | 0.964 | 0.967 | 6.5 | 4.5 |
| 800 | 0.963 | 0.966 | 12.2 | 8.5 | 0.954 | 0.965 | 6.1 | 4.2 |
| 600 | 0.961 | 0.962 | 11.3 | 7.9 | 0.961 | 0.964 | 5.0 | 3.9 |
| 400 | 0.953 | 0.954 | 10.6 | 7.2 | 0.951 | 0.955 | 4.4 | 3.4 |
| 200 | 0.921 | 0.919 | 9.6 | 6.4 | 0.923 | 0.928 | 2.8 | 2.8 |
| 150 | 0.898 | 0.898 | 9.6 | 6.1 | 0.903 | 0.907 | 2.5 | 2.6 |
| 100 | 0.853 | 0.854 | 8.9 | 5.8 | 0.858 | 0.871 | 2.1 | 2.2 |
| 80 | 0.787 | 0.832 | 8.5 | 5.6 | 0.802 | 0.842 | 1.3 | 2.1 |
| 60 | 0.764 | 0.765 | 8.3 | 5.3 | 0.705 | 0.805 | 1.1 | 1.8 |
| 40 | 0.627 | 0.598 | 8.0 | 4.9 | 0.633 | 0.724 | 0.5 | 1.4 |

| | Run 3. 3/32 in. Sphere Pack Temperature 100°F | | | | Run 8. 1 mm. Sphere Pack Temperature 100°F | | | |
|---|---|---|---|---|---|---|---|---|
| | Mole Frac. $CH_4$ | | Liquid Volume | | Mole Frac. $CH_4$ | | Liquid Volume | |
| Press. Psia | Unpack- ed Cell | Packed Cell | Meas. % | Calc. % | Unpack- ed Cell | Packed Cell | Meas. % | Calc. % |
| Initial | 0.935 | 0.937 | 0.0 | 0.0 | 0.936 | 0.936 | 0.0 | 0.0 |
| 2250 | 0.936 | | 0.0 | 0.0 | 0.936 | 0.936 | 0.0 | 0.0 |
| 2000 | 0.935 | 0.938 | 0.0 | 0.0 | 0.936 | 0.936 | 0.0 | 0.0 |
| 1750 | 0.946 | 0.946 | 1.11 | 0.90 | 0.942 | 0.947 | 1.29 | 0.74 |
| 1500 | 0.954 | 0.955 | 2.22 | 1.36 | 0.951 | 0.955 | 1.94 | 1.22 |
| 1250 | 0.957 | 0.959 | 2.69 | 1.51 | 0.957 | 0.957 | 2.10 | 1.39 |
| 1000 | 0.960 | 0.962 | 2.06 | 1.50 | 0.960 | 0.958 | 1.77 | 1.39 |
| 800 | 0.961 | 0.961 | 2.22 | 1.39 | 0.960 | 0.958 | 1.29 | 1.29 |
| 600 | 0.959 | 0.958 | 1.11 | 1.20 | 0.958 | 0.960 | 0.65 | 1.10 |
| 400 | 0.950 | 0.950 | 0.79 | 0.90 | 0.948 | 0.954 | 0.48 | 0.80 |
| 200 | 0.915 | 0.941 | 0.79 | 0.30 | 0.915 | 0.928 | 0.32 | 0.22 |
| 150 | 0.889 | 0.942 | 0.95 | 0.11 | 0.891 | 0.920 | 0.16 | 0.02 |
| 100 | 0.840 | 0.924 | 0.63 | 0.0 | 0.837 | 0.844 | 0.0 | 0.0 |
| 80 | 0.802 | 0.908 | 0.0 | | 0.810 | 0.909 | 0.0 | |
| 60 | 0.746 | 0.886 | | | 0.758 | 0.789 | | |

TABLE 3-3 (Cont.)

## COMPOSITION AND PER CENT LIQUID DATA FOR
## METHANE AND N-PENTANE MIXTURES

Run 10.  1 mm. Sphere Pack  Temperature 100°F    Run 12.  1 mm. Sphere Pack  Temperature 100°F

| Press. Psia | Mole Frac. $CH_4$ Unpacked Cell | Packed Cell | Liquid Volume Meas. % | Calc. % | Mole Frac. $CH_4$ Unpacked Cell | Packed Cell | Liquid Volume Meas. % | Calc. % |
|---|---|---|---|---|---|---|---|---|
| Initial | 0.925 | 0.927 | 0.0 | 0.0 | 0.927 | 0.929 | 0.0 | 0.0 |
| 2000 | 0.931 | 0.931 | 0.48 | 0.40 | 0.932 | 0.933 | Trace | 0.0 |
| 1750 | 0.946 | 0.944 | 2.90 | 2.53 | 0.946 | 0.946 | 2.26 | 2.17 |
| 1500 | 0.952 | 0.952 | 3.39 | 2.78 | 0.954 | 0.955 | 3.23 | 2.47 |
| 1250 | 0.957 | 0.959 | 3.55 | 2.79 | 0.960 | 0.960 | 2.74 | 2.50 |
| 1000 | 0.959 | 0.962 | 3.23 | 2.66 | 0.961 | 0.963 | 2.42 | 2.41 |
| 800 | 0.958 | 0.961 | 3.06 | 2.48 | 0.961 | 0.963 | 2.10 | 2.24 |
| 600 | 0.960 | 0.957 | 2.74 | 2.22 | 0.959 | 0.963 | 1.77 | 2.00 |
| 400 | 0.948 | 0.956 | 1.61 | 1.86 | 0.949 | 0.958 | 1.13 | 1.65 |
| 200 | 0.909 | 0.940 | 0.97 | 1.21 | 0.914 | 0.949 | 0.65 | 1.01 |
| 150 | 0.903 | 0.951 | 0.48 | 1.01 | 0.892 | 0.943 | 0.48 | 0.81 |
| 100 | 0.834 | 0.947 | 0.32 | 0.70 | 0.841 | 0.934 | 0.16 | 0.50 |
| 80 | 0.820 | 0.895 | 0.24 | 0.54 | 0.800 | 0.852 | 0.08 | 0.35 |
| 60 | 0.734 | 0.892 | 0.16 | 0.31 | 0.739 | 0.832 | 0.0 | 0.12 |
| 40 | 0.632 | 0.684 | 0.0 | 0.0 | 0.614 | 0.760 | 0.0 | 0.0 |

Run 9.  1 mm. Sphere Pack  Temperature 100°F    Run 11.  1 mm. Sphere Pack  Temperature 160°F

| Press. Psia | Mole Frac. $CH_4$ Unpacked Cell | Packed Cell | Liquid Volume Meas. % | Calc. % | Mole Frac. $CH_4$ Unpacked Cell | Packed Cell | Liquid Volume Meas. % | Calc. % |
|---|---|---|---|---|---|---|---|---|
| Initial | 0.878 | 0.877 | 0.0 | 0.0 | 0.882 | 0.882 | 0.0 | 0.0 |
| 2250 | 0.901 | 0.898 | 11.1 | 12.0 | 0.882 | 0.881 | 0.0 | 0.0 |
| 2000 | 0.931 | 0.931 | 16.5 | 12.4 | 0.880 | 0.882 | 0.0 | 0.0 |
| 1750 | 0.947 | 0.944 | 16.6 | 12.3 | 0.900 | 0.897 | 2.90 | 1.48 |
| 1500 | 0.955 | 0.953 | 15.7 | 11.3 | 0.909 | 0.910 | 3.87 | 1.90 |
| 1250 | 0.959 | 0.958 | 15.0 | 10.4 | 0.915 | 0.916 | 3.71 | 1.75 |
| 1000 | 0.962 | 0.962 | 13.7 | 9.6 | 0.915 | 0.916 | 3.23 | 1.50 |
| 800 | 0.962 | 0.963 | 13.1 | 8.9 | 0.910 | | 2.58 | 1.17 |
| 600 | 0.958 | 0.959 | 11.8 | 8.3 | 0.897 | | 1.61 | 0.68 |
| 400 | 0.948 | 0.957 | 10.8 | 7.6 | 0.867 | | 0.32 | 0.0 |
| 200 | 0.914 | 0.949 | 10.0 | 6.6 | 0.788 | | 0.0 | 0.0 |
| 150 | 0.890 | 0.893 | 9.2 | 6.4 | | | | |
| 100 | 0.832 | 0.844 | 8.7 | 6.0 | | | | |
| 80 | 0.790 | 0.803 | 8.1 | 5.8 | | | | |
| 60 | 0.715 | 0.740 | 7.4 | 5.5 | | | | |

unpacked cells in Runs 1 and 2 were depleted over ten hour intervals with equilibration (mercury and liquid splashing) times of approximately 20 minutes prior to taking samples. The packed cells in Runs 1 and 2 were depleted over 16 and 13 hour intervals, respectively. There is good agreement between unpacked and packed cell vapor compositions in Run 1, particularly in view of the high liquid saturations. The slightly shorter packed cell depletion time for Run 2 seems to have caused a disproportionate increase in the differences between compositions of the produced vapor.

Runs 3 and 8 had nearly the same initial compositions, but different sized sphere packs. Equilibrium was maintained between phases in both runs at pressures down to about 400 psia. Departures from equilibrium at pressures below 400 psia were the largest in Run 3 which had the smaller interfacial surface area because of the larger sphere size. The depletion times for the packed cells in Runs 3 and 8 were 17 and 19 hours respectively, with both unpacked cells depleted over 12 hour intervals. It may be noted that changes in vapor composition continued after there was no visible liquid in the unpacked cell. Liquid was apparently adsorbed on the walls and in the interstices of the confining cells. This wetting of the walls contributed to the difficulty in obtaining reliable per cent liquid values, especially at the lower liquid saturations.

The depletion times for the packed cells in Runs 10 and 12 were increased to 20 and 27 hours, respectively, however departures from equilibrium were not decreased. Thus it

may be concluded that the formation of new surface area by agitation in the unpacked cell is much more effective for mass transfer than longer time periods with forced convection of the vapor phase in the packed cell.

The high liquid saturations of Run 9 resulted in gravity segregation in the packed cell and non-equilibrium between phases despite a 26 hour depletion time over a period of three days. The higher liquid saturations did, however, result in improved equilibrium for the unpacked cell depletion which was performed in only 11 hours.

Run 11 was performed at $160^O$F and the packed cell was only partially depleted to deposit a liquid saturation for a subsequent vaporization run by contacting with methane. The vaporization run is discussed in Section 3.8.

A comparison of the methane-n-pentane vapor compositions at $100^O$F with other published data is made in Figure 3-3. The results of this work show a critical pressure some 55 psi less than that reported by Sage, Reamer, Olds and Lacey[33], but in good agreement with Wagner and Leach[34] who state that it could not be greater than 2420 psia. The vapor phase compositions are approximately 1.3 per cent richer in methane than those of Sage et al. It should be noted that this relatively small change in equilibrium composition causes very large changes in dew point pressure. The vapor compositions reported by Weinaug and Cordell[4] are also rich in methane compared to the data of Sage et al. The shaded portion of Figure 3-3 shows the region of non-equilibrium data for the packed cell
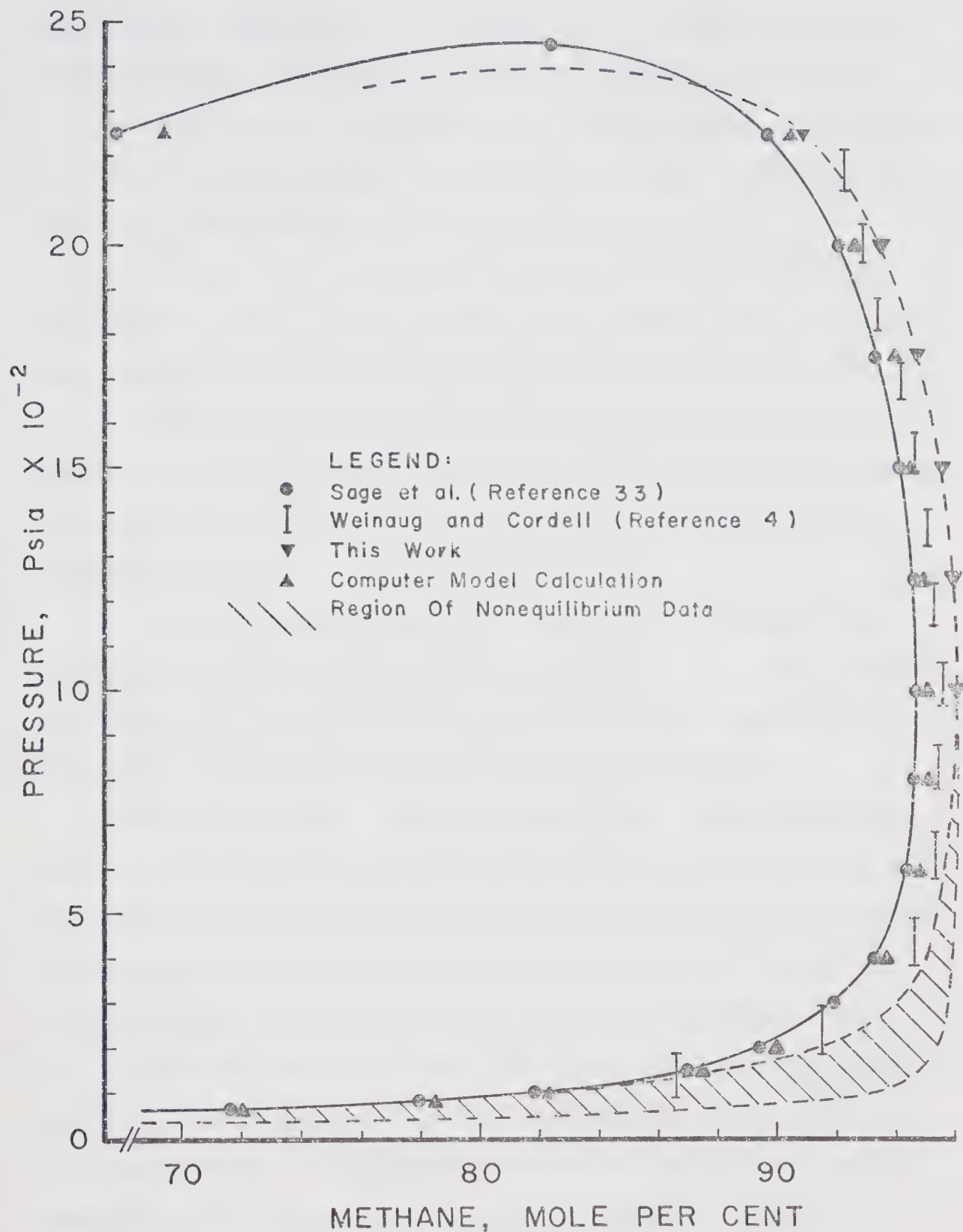
Figure 3-3.   Pressure-Composition Isotherms for the Methane and n-Pentane System at 100°F.

depletions. The data in this region were usually very scattered, however, the following generalizations can be made:

1. Equilibrium was maintained during liquid condensation irrespective of the rate of pressure decrease (often 200 psi/hour), or the diameter of the packing material.

2. During the vaporization portion of the depletion, equilibrium could not be assured even when the rate of pressure decrease in the packed cell was as small as 20 psi/hour.

3. All data (including those of Weinaug and Cordell) indicate that decreasing the diameter of the packing material improves the approach to equilibrium during vaporization by pressure depletion.

4. Forced convection of the vapor phase through the sphere pack did not seem to improve the mass transfer during vaporization. Thus, it would appear that the controlling resistance to mass transfer is in the liquid phase

The comments made in Section 3.3 about the liquid volume data of Table 3-2 also apply to the measured and calculated per cent liquid columns of Table 3-3. The liquid saturations for the differential process used to deplete the packed cell can be estimated from the curves presented in Figure 3-4. This figure was prepared using the vapor compositions shown for this work in Figure 3-3 and the specific volume reported in reference 33. A comparison of Figure 3-4 with Figure 3-2 shows that the reduced volatility of n-pentane delays the vaporization of the retrograde liquid.
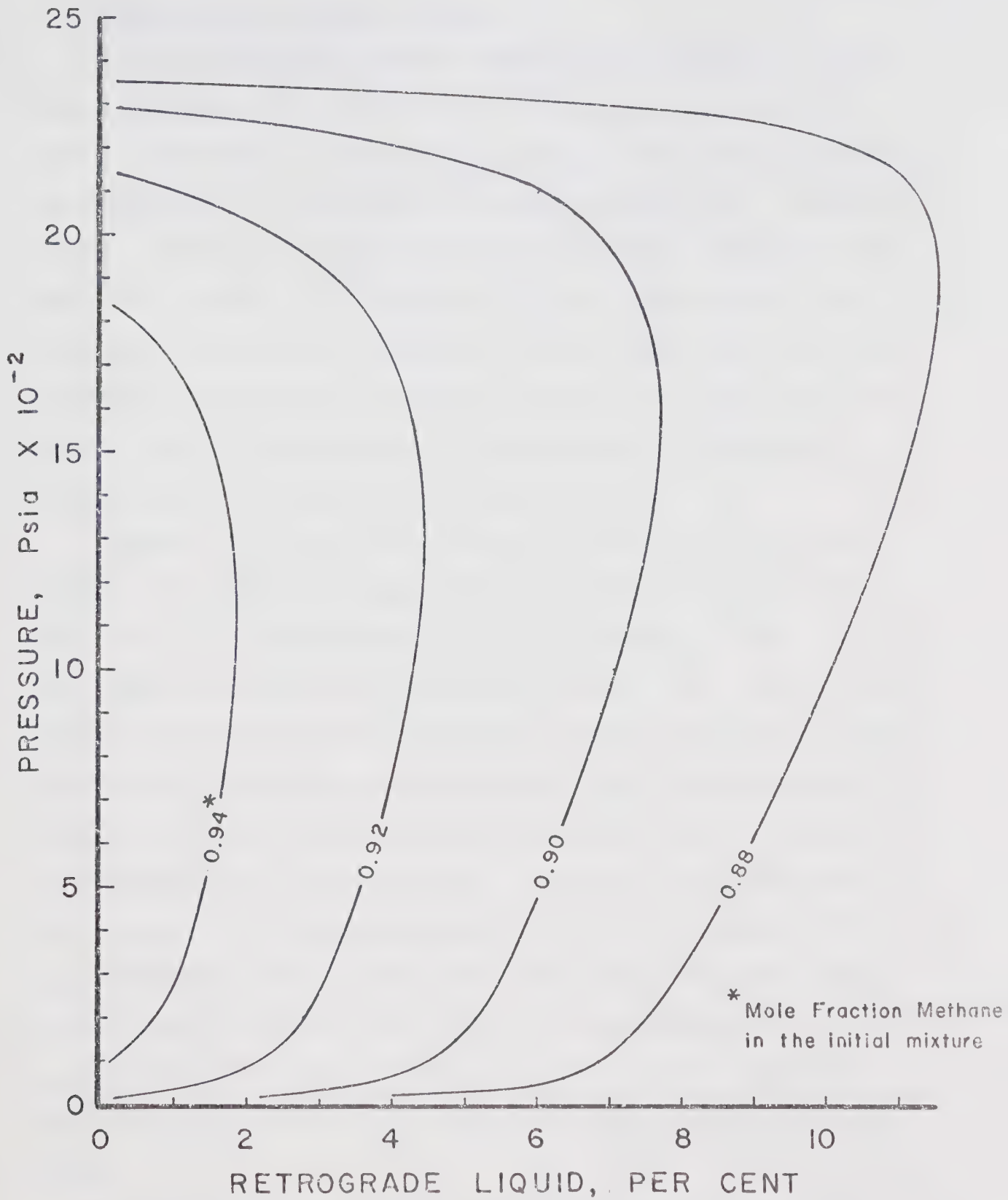
Figure 3-4.   Retrograde Liquid Saturation for Differential
Depletion of Methane-n-Pentane Mixtures.

## 3.5  Methane and n-Hexane Mixture

A single run was made with the methane-n-hexane system
and the results are summarized in Table 3-4.  The unpacked
cell was depleted in one 12 hour period, while the packed cell
was depleted in a total of 24 operating hours over a four day
period.  Table 3-4 indicates relatively small differences be-
tween the unpacked and packed cell vapor compositions, and it
might be concluded that there was little departure from ther-
modynamic equilibrium.  However, reference to Figure 3-5 in-
dicates that it is doubtful if equilibrium was obtained in
either cell at pressures below 1500 psia.

The data of Poston and McKetta[35] shown on Figure 3-5
indicate an unusually sharp reversal of the retrograde dew
point locus to the reported critical pressure of 2902 psia.
The vapor compositions of this work at 2500 psia and 2700 psia
tend to indicate that the pressure-composition diagram should
have more curvature at high pressure.  Other methane-alkane
binaries exhibit a more gradual reversal of the dew point
locus toward the critical state.  A comparison of the data of
Run 7 during the vaporization portion of the depletion with
the equilibrium data of Shim and Kohn[36] indicates that very
little vaporization of the retrograde liquid occured.  The
nearly constant value for the measured per cent liquid in
Table 3-4 confirms that the retrograde liquid vaporized very
slowly.

The conditions for liquid vaporization were the least
favorable in Run 7 since the largest sphere size and the least

## TABLE 3-4

## COMPOSITION AND PER CENT LIQUID DATA FOR
## THE METHANE AND N-HEXANE MIXTURE

Run 7.  3/32 in. Sphere Pack
Temperature 100°F

| Press. Psia | Mole Frac. $CH_4$ Unpacked Cell | Packed Cell | Liquid Volume Meas. % | Calc. % |
|---|---|---|---|---|
| Initial | 0.930 | 0.930 | 0.0 | 0.0 |
| 2750 | 0.936 | | 5.9 | 5.81 |
| 2700 | | 0.946 | | |
| 2500 | 0.960 | 0.959 | 10.1 | 7.02 |
| 2250 | 0.971 | 0.969 | 11.7 | 8.25 |
| 2000 | 0.975 | 0.977 | 11.9 | 8.58 |
| 1750 | 0.984 | 0.979 | 13.7 | 8.24 |
| 1500 | 0.985 | 0.986 | 12.4 | 7.95 |
| 1250 | 0.988 | 0.989 | 12.0 | 7.62 |
| 1000 | 0.988 | 0.990 | 11.2 | 7.27 |
| 800 | 0.990 | 0.989 | 10.8 | 6.96 |
| 600 | 0.988 | 0.988 | 10.4 | 6.64 |
| 400 | 0.985 | 0.986 | 9.9 | 6.29 |
| 200 | 0.975 | 0.980 | 9.2 | 5.85 |
| 100 | 0.954 | 0.956 | 8.8 | 5.53 |
| 50 | 0.894 | 0.910 | 7.9 | 5.27 |
| 25 | 0.690 | 0.715 | 7.5 | 5.02 |
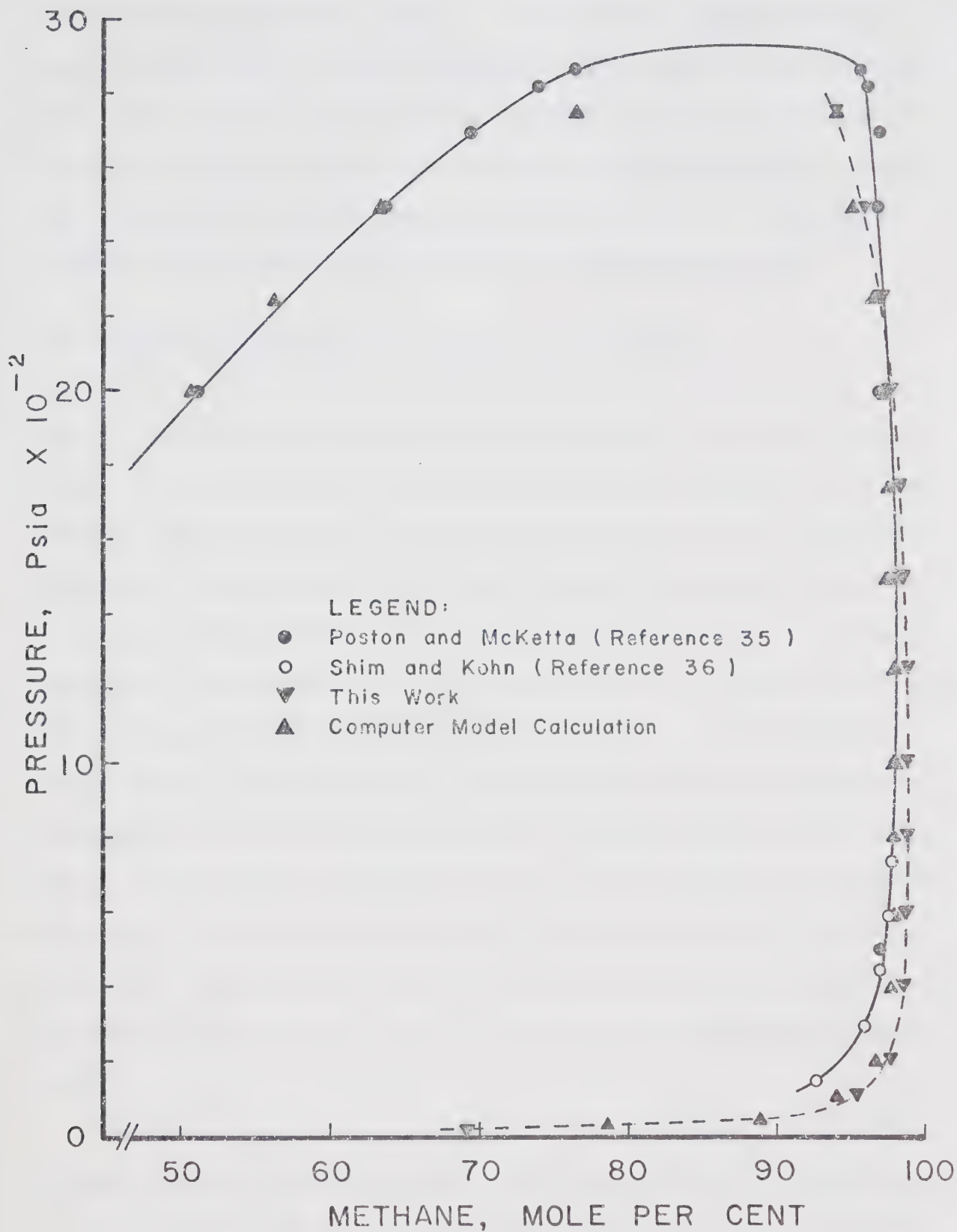
Figure 3-5.  Pressure-Composition Isotherms for the Methane and n-Hexane System at 100°F.

volatile component were used. All evidence suggests that
equilibrium is not readily attained, and that the problem be-
comes more severe with decreased volatility. It may be that
the intermediate components in multicomponent mixtures reduce
the resistance to mass transfer for the heavier components,
however, this would have to be verified by experiment.

## 3.6 Role of Fugacity in Attaining Equilibrium

The previous sections pointed out the difficulty of main-
taining equilibrium during the vaporization portion of deple-
tions. The packed cell depletions were carried out under con-
ditions where material and momentum fluxes existed between
phases so equilibrium in its more general sense was never
attained. The transfer of material between phases involves
transport properties which are assumed to be a function of the
thermodynamic state of the phase at a point. When several
fluxes occur simultaneously, the interrelation of transport
phenomena are given by irreversible thermodynamics. Unfortu-
nately, irreversible thermodynamics has not been sufficiently
developed to permit calculations for phase behavior at high
pressure. The driving force which causes interphase mass
transfer is the fugacity and it needs to be examined in more
detail.

The fugacity of any component i in a phase is a measure
of its escaping tendency, therefore the fugacity of component
i must be the same in all equilibrated phases. The fugacity
of a component depends upon the pressure, temperature and
composition of the system. The total differential of the
fugacity of component i in a system of m components is given

by

$$df_i = \left(\frac{\partial f_i}{\partial P}\right)_{T,x} dP + \left(\frac{\partial f_i}{\partial T}\right)_{P,x} dT + \left(\frac{\partial f_i}{\partial x_j}\right)_{P,T,x_k} dx_j \qquad (3-1)$$

$$k = 1, \ldots, j-1, j+1, \ldots, m-1$$

For a binary mixture the change in fugacity of component i with pressure at constant temperature is given by

$$\left(\frac{\partial f_i}{\partial P}\right)_T = \left(\frac{\partial f_i}{\partial P}\right)_{T,x} + \left(\frac{\partial f_i}{\partial x_j}\right)_{P,T}\left(\frac{dx_j}{dP}\right)_T \qquad (3-2)$$

The derivative on the left side of Equation 3-2 gives the change in the fugacity of component i with pressure for the coexisting phases of a binary mixture. Fugacities have been published[32, 33] for the coexisting phases of the methane-n-butane and methane-n-pentane systems. These data have been replotted and the n-butane and n-pentane fugacities are shown in Figure 3-6. It is apparent that under the experimental conditions of 100°F the fugacities of these two components are nearly invariant with pressure, and that the derivative on the left side of Equation 3-2 will be of small magnitude.

The first term on the right hand side of Equation 3-2 can be evaluated from partial volumetric data by the thermodynamic relation

$$\left(\frac{\partial \ln(f_i)}{\partial P}\right)_{T,P} = \frac{v_i}{RT} \qquad (3-3)$$

The second term on the right hand side involves the product of two derivatives. The first derivative is of particular interest since it shows how fugacity changes with composition at constant temperature and pressure. Thus, when the
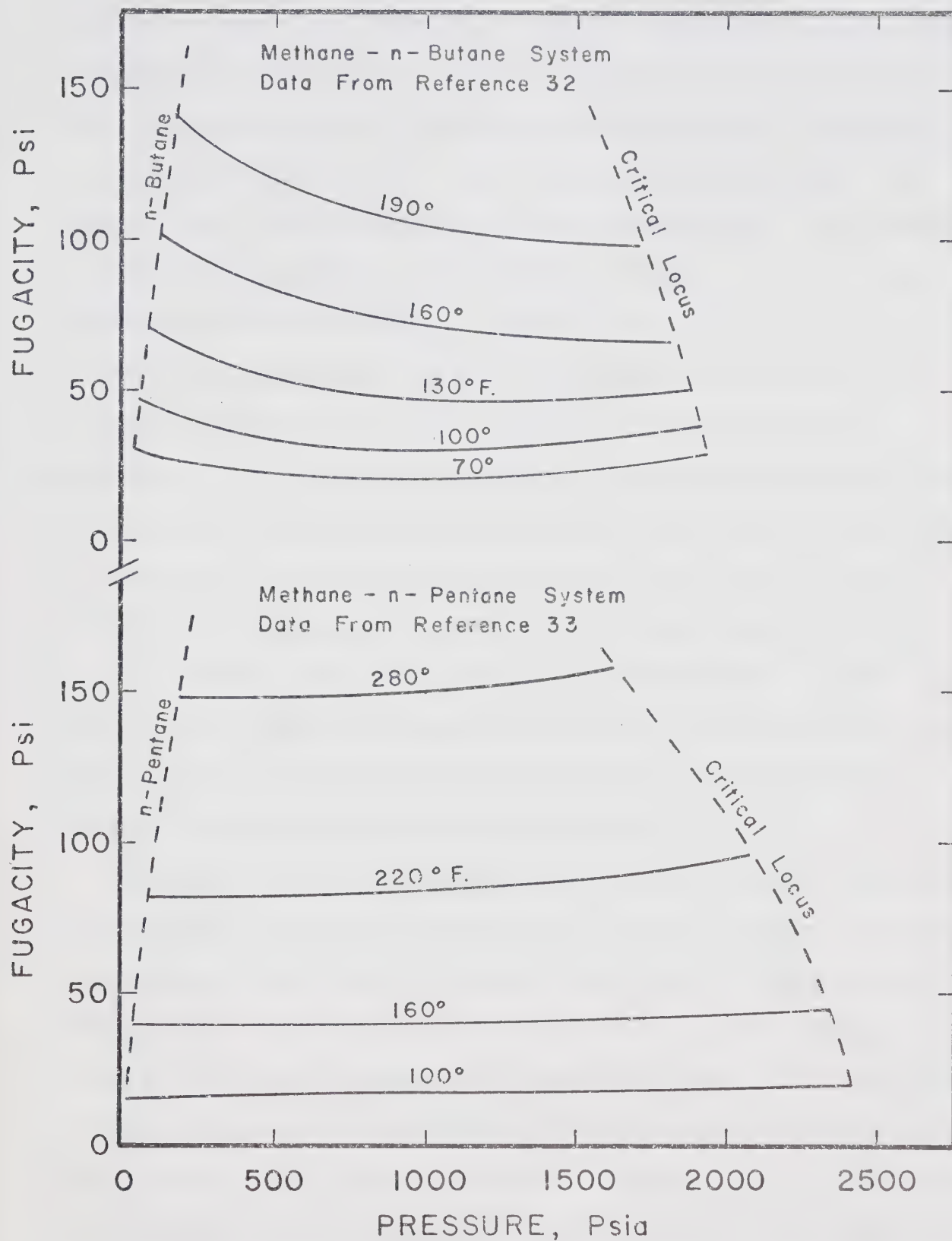
Figure 3-6.   Examples Showing the Effect of Pressure on
Fugacity in the Two Phase Region.

coexisting vapor and liquid are not in equilibrium (i.e. the composition is perturbed from the equilibrium value) this term gives the magnitude of the driving force for mass transfer to re-establish equilibrium. The second derivative gives the change in the coexisting equilibrium composition with pressure and can be evaluated by constructing tangents to a pressure-composition isotherm such as Figure 3-1.

The following results are presented even though it is clearly hazardous to evaluate some of the derivatives in Equation 3-2 by graphical methods. The extensive tables for the methane-n-butane system in references 32 and 37 were used to calculate the effect of composition upon the fugacity of n-butane. The derivative $(\partial f_i / \partial x_j)_{T,P}$ was calculated for both the liquid and vapor phases at temperatures of 100°F and 160°F. The results of these calculations are shown in Figure 3-7, and their significance with respect to establishing equilibrium may be explained as follows.

Consider the coexisting phases during a typical depletion run at 100°F. The mass transfer of n-butane during the pressure interval from the retrograde dew point to approximately 1000 psia is from the vapor (donor phase) to the liquid. During this pressure interval the curves of Figure 3-7 show that any departure of the vapor phase from the equilibrium composition causes a much larger change in fugacity than a corresponding departure from equilibrium in the liquid phase. Thus, the tendency is for both phases to stay very close to equilibrium. However, at pressures below 1000 psia n-butane is transferred
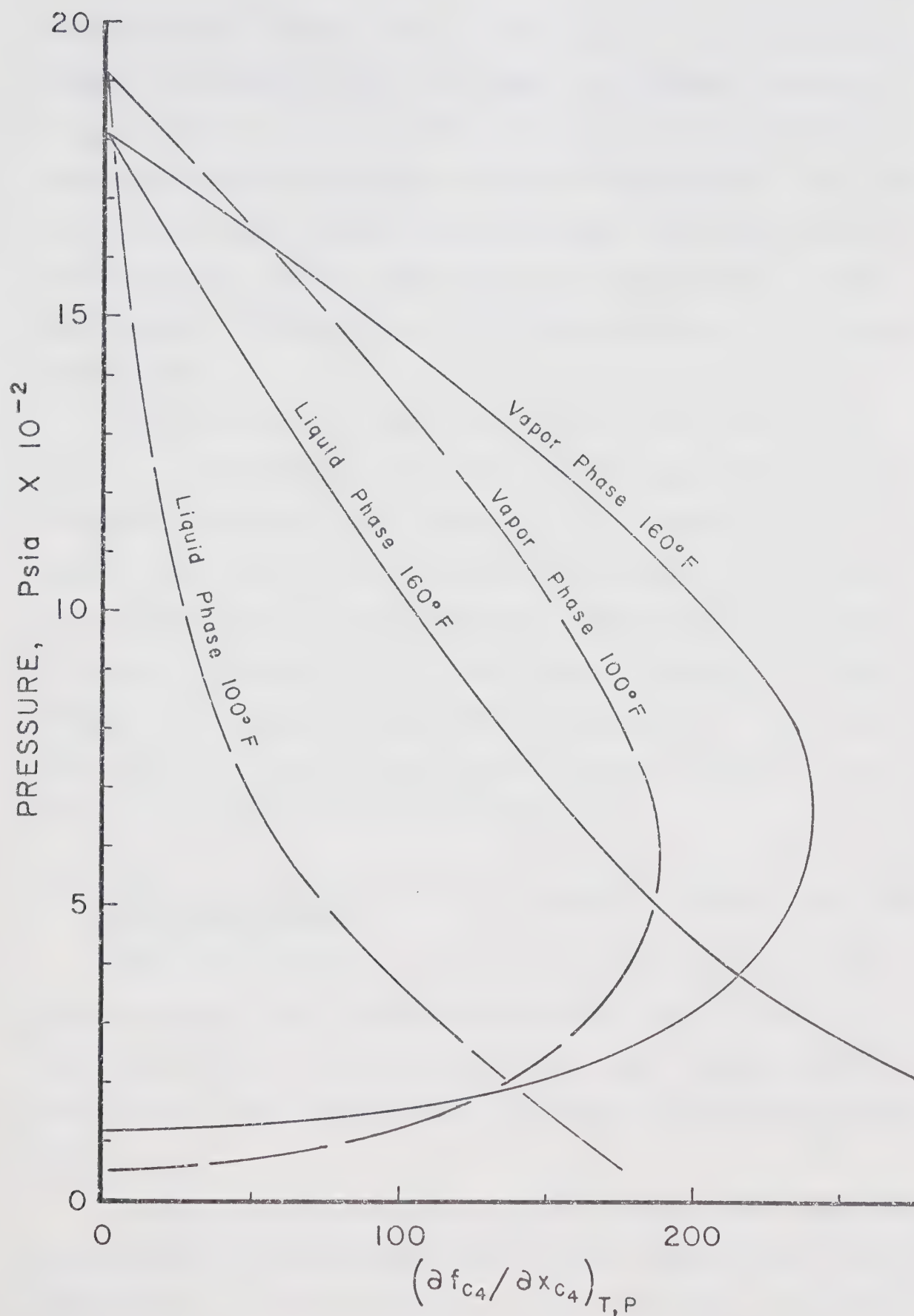
Figure 3-7.  Effect of Composition on the Fugacity of
            n-Butane in the Two Phase Region.

from the liquid (donor phase) to the vapor. In the pressure interval from 1000 psia to 200 psia the tendency is towards non-equilibrium since the donor phase is not as sensitive to departures from equilibrium as the receiving phase. At pressures below 200 psia conditions are again favorable for equilibrium because of the rapid decline in sensitivity of the vapor phase to composition as the vapor pressure of n-butane is approached.

The conditions at 160°F in Figure 3-7 are similar to those at 100°F except that the point of equal sensitivity of the phases to composition occurs at approximately 375 psia instead of 200 psia. Thus, the pressure interval where there is a tendency to non-equilibrium is considerably smaller at the higher temperatures. If the trend continued for higher temperatures one might expect that supercritical components would exhibit a tendency to non-equilibrium during condensation, and equilibrium during vaporization.

## 3.7  Simultaneous Packed Cell and Unpacked Cell Dew or Bubble Point Measurements

Table 3-5 summarizes the simultaneous retrograde dew point or bubble point determinations in a pack of 30-40 U.S. Mesh glass beads. Any observed differences between packed and unpacked cells were within the limits of the experimental error.

For compositions near the critical state, dark opalescence was observed in the unpacked cell as the critical point was approached. The data in Table 3-5 are the basis for drawing

TABLE 3-5

SIMULTANEOUS PACKED CELL AND UNPACKED CELL DEW
OR BUBBLE POINT MEASUREMENTS

System:   Methane and n-Pentane at 100°F

Pack:     30-40 U.S. Mesh Glass Beads

| Composition Mole Frac. Methane | Dew (Bubble) Point Press., Psia | | Remarks |
| | Unpacked Cell | Packed Cell | |
| --- | --- | --- | --- |
| 0.899 | 2335 | 2335 | Dew Point |
| 0.783 | 2392 | 2392 | Bubble Point |
| 0.808 | 2395 | 2396 | Bubble Point |
| 0.827 | 2398 | 2399 | Dark Opalescence |
| 0.835 | 2398 | 2398 | Dew Point |
| 0.846 | 2401 | 2401 | Dew Point |
| 0.768 | 2356 | 2356 | Bubble Point |
| 0.820 | 2390 | 2390 | Dark Opalescence |
| 0.862 | 2376 | 2376 | Dew Point |
| 0.888 | 2341 | 2341 | Dew Point |
| 0.922 | 2200 | 2200 | Dew Point |

the pressure-composition isotherm in Figure 3-3 some 55 psi
below the critical point reported in reference 33.

On the basis of a theoretical study by Morrow et al.[26],
in which curvature effects at the vapor-liquid interface were
investigated using a thermodynamic model, it was concluded
that unless the particle size was less than a few microns,
curvature effects on equilibrium pressures are negligible.  It
was also concluded that although reservoir rocks may contain a
large proportion of fine pores, these pores would not be avail-
able to  retrograde liquids since they would be occupied by
formation water.

Therefore all the evidence of this work is that curvature
effects on equilibrium pressures and compositions are neglig-
ible.  The reported anomalous phase behavior in porous media
discussed in Section 1.4 probably results from lack of equilib-
rium and/or from more than one flux operating so that meaning-
ful interpretation lies in the field of irreversible thermo-
dynamics.

## 3.8  Vaporization of a Retrograde Liquid by Contacting with Methane

The retrograde liquid saturation in the 1 mm. sphere pack
of Run 11 was vaporized by contacting with methane at 1000 psia
and 160°F.  Figure 3-8 shows the mole percentage of n-pentane
in the effluent from the packed cell versus pore volumes of
injected methane.  The results are qualitative since this was
a shakedown run to test the apparatus for vaporization experi-
ments.  A slight increase in the n-pentane content of the
effluent was observed just prior to breakthrough.  A similar
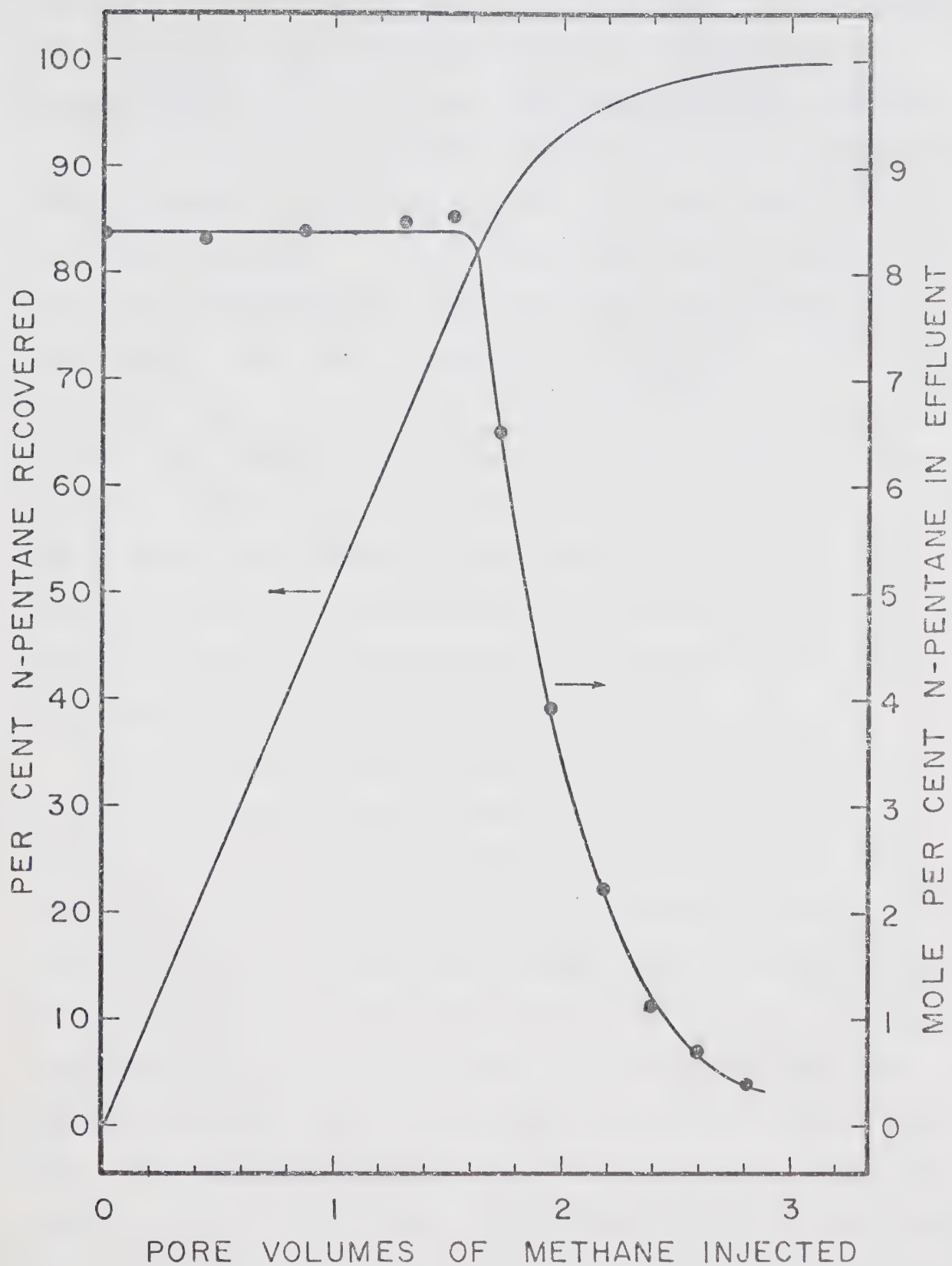
Figure 3-8.  Pentane Recovery by Contacting with Methane.

increase was observed by Smith and Yarborough[13], so it appears that a slightly enriched zone preceding breakthrough is a characteristic of the constant pressure vaporization process.

The decrease in n-pentane concentration after breakthrough shown in Figure 3-8 was not as abrupt as those observed by Smith and Yarborough[13] for an Ottawa sand pack. This may have been due to channeling in the relatively coarse 1 mm. sphere pack used in this work, or because of unfavorable cell geometry. The length to cross-sectional area ratio was 17.7 cm.$^{-1}$ in this work compared to 43.1 cm.$^{-1}$ for the apparatus used by Smith and Yarborough. Figure 3-8 indicates a mixing zone (zone during which the n-pentane concentration in the effluent decreases to zero) in excess of one pore volume, whereas mixing zones of some 0.25 pore volumes were reported by Smith and Yarborough.

The curve of per cent n-pentane recovered versus pore volumes of methane injected shown in Figure 3-8 was plotted so that 100 per cent corresponds to a calculated n-pentane recovery of $25.6 \times 10^{-6}$ moles. If the measured liquid saturation of 3.23 per cent for the unpacked cell depletion is applied to the packed cell, then there were $22.2 \times 10^{-6}$ moles of n-pentane in the pack at the start of the vaporization run indicating a discrepancy of 13.3 per cent in the material balance. The density data of Sage, Reamer, Olds and Lacey[33] were used for these calculations. These data may not be applicable since the composition of the vapor phase in Run 11 was approximately two mole per cent richer in methane than the corresponding data of Sage et al.

3.9  Photographs of Retrograde Liquid Structures

Photographs of condensed liquid structures were taken with a standard 35 millimeter camera equipped with an extension tube for increased magnification. Various exposure settings, film speeds, lighting arrangements and sphere sizes were tried in order to obtain satisfactory photographs of the liquid rings which formed at the contact points between the packing spheres and the window of the Jerguson cell.

Based on the theoretical analysis of Morrow et al.[26] it was concluded that the curvatures developed in sphere packs used in this work would have a negligible effect upon phase behavior. Having regard for this, and the fact that photograph quality improved with increased sphere size, several runs were made with 3/32 inch diameter sphere packs. Figure 3-9 shows two photographs of the same sphere pack; one at a pressure above the retrograde dew point without a retrograde liquid saturation, and another in the two-phase region with a retrograde liquid saturation.

Photographs were taken at regular pressure intervals during the packed cell depletions. The diameter of the liquid rings could be observed to increase as the pressure was decreased from the retrograde dew point to some intermediate pressure below which the diameter of the liquid rings would decrease as the liquid vaporized. If a particular composition resulted in too much retrograde liquid, the rings would grow until they joined together causing gravity segregation which retarded vaporization of the liquid. Suites of photographs for several runs are shown in Appendix I.
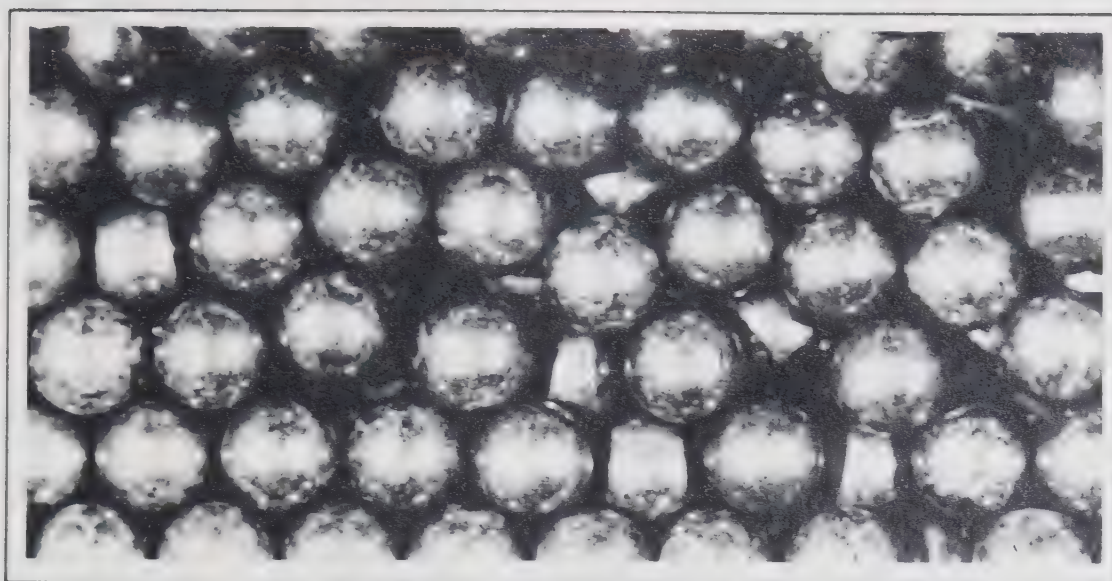
PHOTOGRAPH OF A 3/32 in. DIAMETER SPHERE PACK
WITHOUT A RETROGRADE LIQUID SATURATION
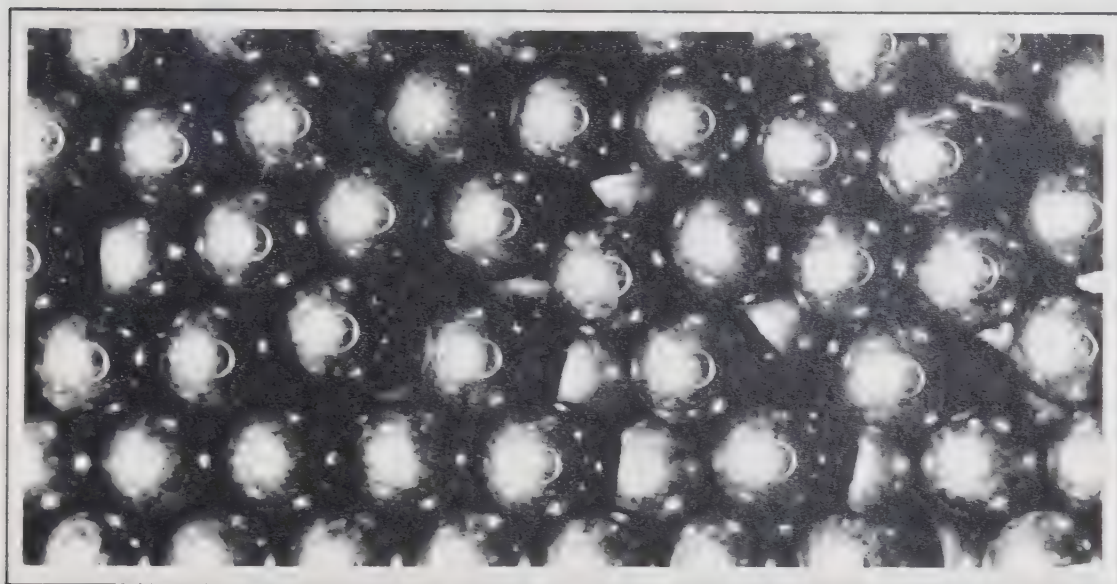


PHOTOGRAPH OF THE SAME SPHERE PACK SHOWING RETROGRADE
LIQUID RINGS WHERE THE SPHERES CONTACT THE CELL WINDOW

Figure 3-9.   Typical Photographs of Sphere Packs.

Chapter 4.   CALCULATION OF VAPOR-LIQUID EQUILIBRIA

## 4.1   Foreword

The reservoir engineer would like to be able to predict
and compare the performances, fluid recoveries and resulting
cash flows for various exploitation schemes.  In order to be
able to make these predictions, the composition and density
of the vapor and liquid phases are required as functions of
pressure.  The vapor-liquid equilibria and density data for
reservoir fluids are usually obtained from laboratory experi-
ments.  There is, however, a trend to use a digital computer
to calculate these data starting with the initial composition
and a minimum of laboratory data.  These calculations require
equilibrium ratios for every component and a suitable density
correlation for the coexisting phases.

Equilibrium ratios, or K-values as they are more often
called, are defined as the ratio of the mole fraction of com-
ponent i in the vapor phase, $y_i$, to the mole fraction of the
same component in the liquid phase, $x_i$, hence

$$K_i = y_i/x_i \tag{4-1}$$

These ratios are known to be functions of temperature, pressure
and system composition.  The common methods of correlating
and calculating K-values are reviewed in this chapter.

## 4.2   The N.G.A.A. K-value Charts

The Natural Gasoline Association of America (N.G.A.A.)
has  prepared several different series of K-value charts for
the normal alkanes.  The first series was published in the

1951 N.G.S.M.A. Engineering Data Book[38] for pressures up to 800 psia. These charts were based on the fugacity tables of W. K. Lewis of the Massachusetts Institute of Technology.

In 1945 Hanson and Brown[39] compared the behavior of some mixtures containing light hydrocarbons which were selected to have critical pressures at the operating temperature. K-values for these mixtures could be measured for all pressures up to the critical where they were all observed to converge to unity. Thus, the "convergence pressure" was taken to be the pressure at which the K-values on a plot of log $K_i$ versus log P converged to unity. For a binary mixture the convergence pressure, $P_k$, is exactly equal to the critical pressure. Hanson and Brown also observed that the K-value for a partic-ular component at a specified temperature and pressure was the same in different mixtures provided the mixtures had the same convergence pressure. This meant that the effect of composition on K-values could be accounted for by the conver-gence pressure concept. Based on this finding, the N.G.A.A. started to use convergence pressure as a correlating parame-ter. The 1957 N.G.S.M.A. Engineering Data Book[40] contained K-value charts for convergence pressures of 600, 800, 1000, 2000, 3000, 4000, 5000, 10000 and 20000 psia. The latest series was published in the 1966 N.G.P.A. Engineering Data Book[41] and charts are provided for convergence pressures of 800, 1000, 2000, 4000 and 10000 psia. The number of conver-gence pressures covered by the latest series was reduced due to the lack of internal consistency in the earlier charts and the increased popularity of equation of state type

correlations which are easily programmed for computer solution.

In order to adapt the charts in the 1957 N.G.S.M.A. Data Book for computer usage K-values were approximated by the functional form

$$\ln(K_{ij} \, P) = \frac{1000}{T} \sum_{m=1}^{4} \sum_{n=1}^{7} A_{mnij} \left(\frac{T}{1000}\right)^{m-1} \left(\frac{\ln P}{10}\right)^{n-1} \quad (4-2)$$

where: $K_{ij}$ is the K-value for component i at convergence pressure j,

$A_{mnij}$ are the N.G.P.A. curve fit coefficients for component i at convergence pressure j,

P is the system pressure, psia,

T is the system temperature, °R.

The K-values evaluated from the N.G.P.A. coefficient deck[42] deviate considerably from the charts when the ratio $P/P_k >$ 0.9. Schlaudt[43] extended the surface fit to cover this region by assuming a linear relationship between log $K_i$ and log P in the range $0.9 < P/P_k < 1.0$. The analytical representation for this range of pressure is

$$K_i = \left(P/P_k\right)^{\left(\log(K_{i,P/P_k=0.9})/\log(0.9)\right)} \quad (4-3)$$

where: $K_{i,P/P_k=0.9}$ is the K-value of component i at the pressure ratio $P/P_k=0.9$

Since the convergence pressure is not a parameter in Equation 4-2 a suitable means for interpolation is required to calculate K-values for a specific convergence pressure. Figure 4-1 shows the K-values for the methane-n-pentane system at 100°F for convergence pressures of 600, 800, 1000, 1500, 2000, 3000 and 5000 psia. This figure shows that
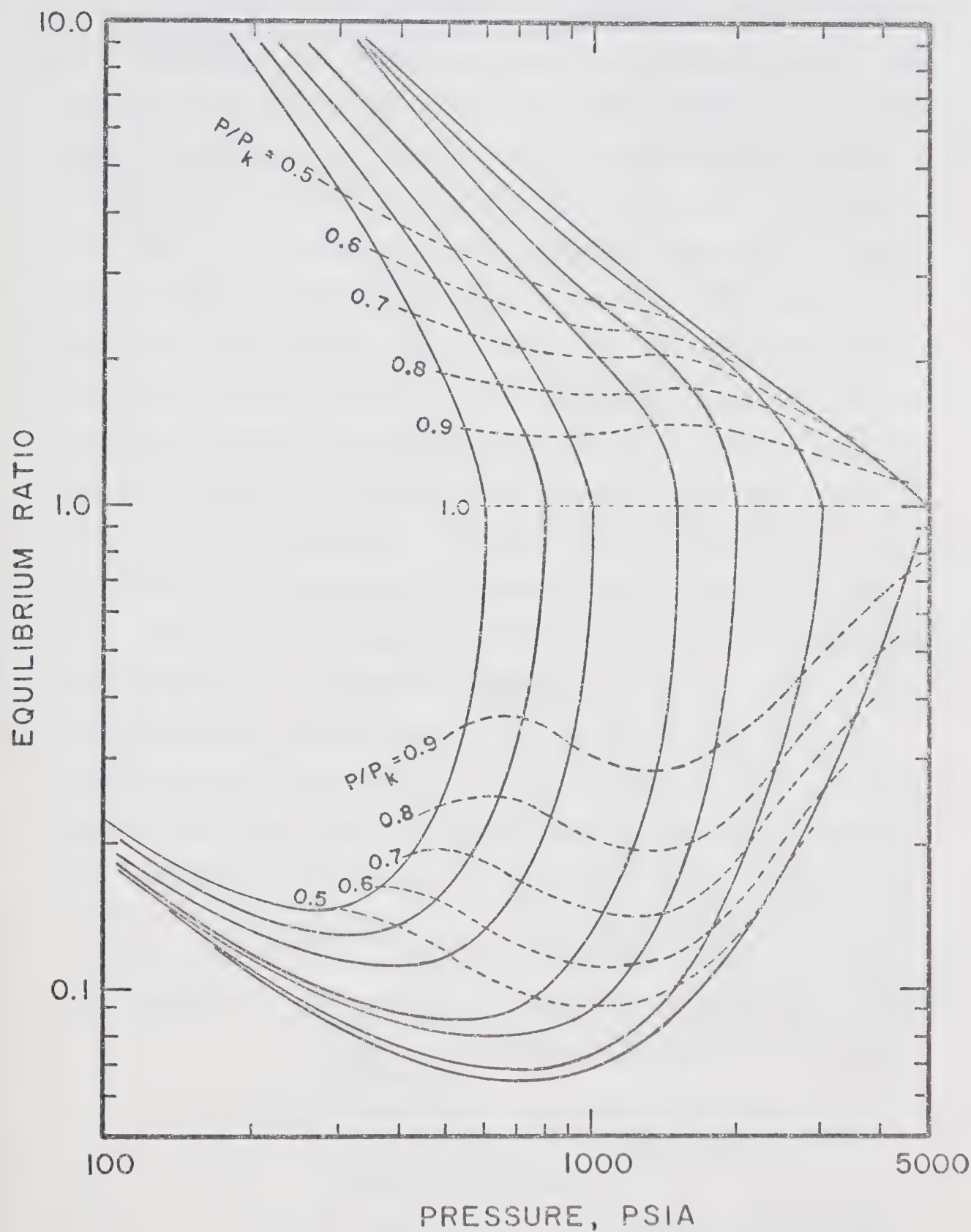
Figure 4-1. Equilibrium Ratios for the Methane-n-Pentane System at 100°F.

K-values are a strong function of composition (hence conver-
gence pressure) for conditions near the critical state. Sup-
pose that the K-value for n-pentane was required for a pres-
sure of 1200 psia in a mixture with a convergence pressure
of 1500 psia. Since a curve for $P_k$ = 1500 psia is provided
the value of 0.194 can be read directly. However, if the
curve or corresponding surface fit for $P_k$ = 1500 psia was not
available, the K-value would have to be extrapolated from the
K-value(s) corresponding to the next higher available conver-
gence pressure(s). Extrapolation is required since K-values
are not defined for convergence pressures which are less
than the system pressure. Interpolation rather than extrapo-
lation may be applied by an approach which uses the ratio
$P/P_k$. This ratio is used to evaluate K-values for the avail-
able convergence pressures above and below the system conver-
gence pressure. The dashed curves in Figure 4-1 give the
loci of several $P/P_k$ ratios. If it is assumed that the $P/P_k$
locus between two adjacent convergence pressures is linear
then the following interpolation formula can be used.

$$K_i = K_{i,1} \exp\left(\ln(K_{i,2}/K_{i,1})\ln(P_k/P_{k,1})/\ln(P_{k,2}/P_{k,1})\right)$$

(4-4)

where: $P_{k,1}$ is the first available convergence
pressure from the N.G.P.A. correlation
which is less than the system convergence
pressure,

$P_{k,2}$ is the first available convergence
pressure from the N.G.P.A. correlation
which is greater than the system
convergence pressure,

$K_{i,1}$ is the K-value for component i evaluated
at $P = (P/P_k)P_{k,1}$ and system temperature,

$K_{i,2}$ is the K-value for component i evaluated
at $P = (P/P_k)P_{k,2}$ and system temperature.

Equations 4-3 and 4-4 may be used with fair success in the pressure range from $0.5 < P_k < 1.0$. The use of Equation 4-4 at pressures less than $0.5 P_k$ leads to large errors. Attempts to develop a single interpolation formula which could be applied over the full pressure range were unsuccessful. Interpolation schemes which used a combination of separate formulas lacked internal consistency as the change over point between formulas could be detected when the K-values were plotted. For these reasons the N.G.A.A. charts and approximating functions were not used in any of the phase simulation calculations in this work.

To this point no mention has been given to how the convergence pressure for a particular mixture may be calculated. The method of Hadden[44] is frequently used, and is recommended in the 1957 N.G.S.M.A. Engineering Data Book and the 1966 N.G.P.S.A. Engineering Data Book. In Hadden's method the convergence pressure is taken to be the critical pressure of a pseudo-binary mixture at the system temperature. The pseudo-binary mixture is composed of the most volatile component present in the mixture and a pseudo-heavy component comprising a weight average of all the components in the liquid phase except the most volatile component. The method is well-suited for hand calculations, but would be difficult to program for computer usage. A more rigorous method which can be adapted for computer use is considered in the next section.

## 4.3 The Critical Composition Method of Estimating Convergence Pressure

Rowe[29] presented a critical composition method which is a logical extension of the convergence pressure concept from binary to ternary, and from ternary to multicomponent mixtures. Rowe defined the convergence pressure to be "the critical pressure of a critical mixture which, when flashed to the operating pressure, will result in a tie line that passes through the over-all system composition for which the K-values are desired". The method is a trial and error procedure. First a convergence pressure is assumed so that K-values can be obtained from a correlation. Then flash calculations are performed to define a tie line from which a new convergence pressure is calculated. The procedure is repeated until the calculated convergence pressure is in good agreement with the convergence pressure used to obtain the K-values.

The critical composition method yields the same convergence pressures as Hadden's method for binary mixtures. However, it may yield significantly different values for convergence pressure in ternary or multicomponent mixtures. Thus, there may be cases where there is an inconsistency in data correlation when the critical composition method is used with existing K-value correlations which were not prepared with this definition of convergence pressure.

The accuracy of the critical composition method depends upon the accuracy of the critical temperature and critical pressure correlations with which it is used. A critical temperature correlation is used to locate the composition

along a tie line which has a critical temperature equal to the system temperature. Grieves and Thodos[45] found the locus of critical temperatures for ternary hydrocarbon mixtures to be linear on a compositional diagram. This fact simplifies the search for the composition of the critical mixture. The composition of the critical mixture is used in a critical pressure correlation to calculate the convergence pressure of the system.

The critical temperatures of paraffin hydrocarbon mixtures lie between the critical temperatures of the pure components. Also, the critical temperatures tend to be symmetric with respect to a composition variable and are therefore easily correlated. Several authors have reported accurate correlations for calculating critical temperatures[46, 47, 48, 49, 50, 51]. The method of Etter and Kay[52] was selected for this work because analytical expressions were provided which could be easily programmed for computer evaluation. This method is described further in Appendix D.

It is considerably more difficult to accurately predict the critical pressures of hydrocarbon mixtures than it is to predict their critical temperatures. Unlike critical temperatures, critical pressures may be much higher than the mole average critical pressure of the mixture. Also, critical pressures are not usually symmetric with respect to composition and may exhibit a sharp maximum, and/or a point of inflection. Several authors have presented critical pressure correlations[46, 47, 49, 50, 51, 53, 54, 55, 56]. The method of

Etter and Kay[52] was selected for this work, again because of the ease with which it could be programmed.  A completely satisfactory critical pressure correlation was not available in the literature.  Since the success of the critical composition method depends upon the accuracy of the critical pressure correlation, some work was done on correlating critical properties.  This work is summarized in Appendix F.

Schlaudt[43] extended the critical composition method to multicomponent systems.  The basis for the extension is best described by considering the pressure-temperature diagram for a two-phase reservoir fluid such as that shown in Figure 4-2. The critical points for the reservoir vapor and liquid phases are shown.  A critical locus is also shown for all combinations of the coexisting vapor and liquid phases.  To apply the critical composition method to this system, various proportions of the vapor and liquid phases are tried until an overall mixture is found which has a critical temperature equal to the reservoir temperature.  The required convergence pressure is then the critical pressure of this mixture.  The lack of dependable correlations for critical properties in multicomponent systems is the only factor preventing the critical composition method from receiving wide usage in natural reservoir systems.

## 4.4  The Chao-Seader Method

In 1961 Chao and Seader[27] published a general correlation for calculating compositionally dependent K-values for hydrocarbon mixtures.  The correlation has received widespread
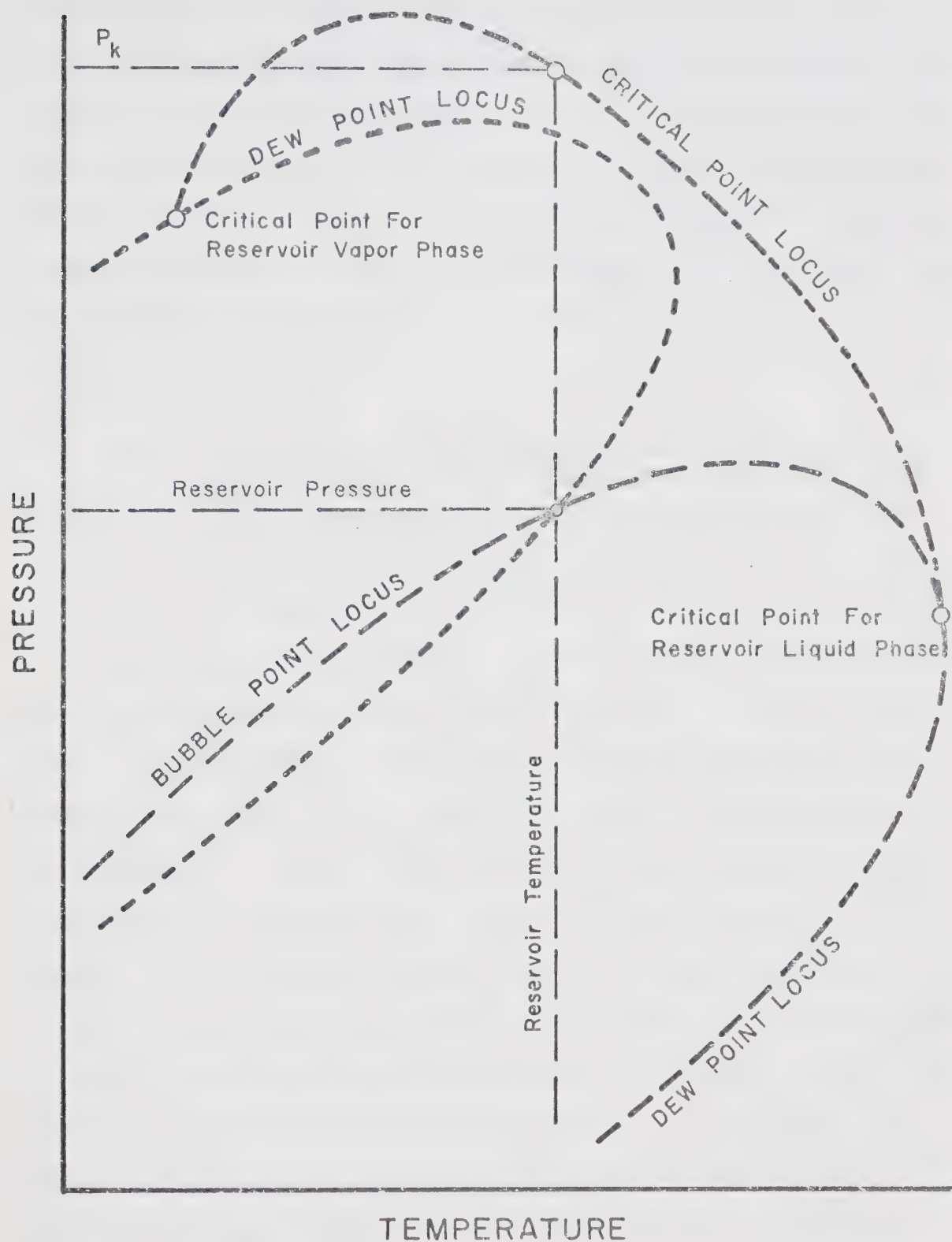
Figure 4-2.  Pressure-Temperature Diagram Illustrating the
Critical Composition Method for Calculating
Convergence Pressure in Multicomponent Systems.

acceptance by the natural gas processing industry. The N.G.P.A. have extended the method to include sour gases, and offer a computer program which also calculates enthalpies for hydrocarbon mixtures. The correlation relates the non-ideal behavior of each component in coexisting phases to the properties of the pure components. K-values are calculated from the following equation

$$K_i = \nu_i \, \gamma_i / \phi_i \qquad (4-5)$$

where: $\nu_i$ is the liquid fugacity coefficient of pure component i at system conditions,

$\gamma_i$ is the activity coefficient for pure component i in the liquid solution,

$\phi_i$ is the vapor fugacity coefficient of pure component i in the vapor mixture.

The liquid phase fugacity coefficient is well defined for any component provided the system pressure is greater than the vapor pressure of the component at system temperature, and the system temperature is less than the critical temperature of the component. Under these conditions the fugacity coefficient can be obtained from a generalized correlation[31, 57]. However, if the system temperature or pressure are such that the pure liquid could not exist, a hypothetical fugacity must be used. Chao and Seader extended the Curl and Pitzer[57] correlation to these hypothetical regions using fugacity coefficients back calculated from experimental vapor-liquid equilibrium data. Thus, fugacity coefficients were correlated by the equation

$$\log \nu_i = \log \nu_i^{(0)} + \omega_i \log \nu_i^{(1)} \qquad (4-6)$$

where: $\nu_i^{(0)}$ is the fugacity coefficient for a simple fluid,

$\nu_i^{(1)}$ is a correction term for the departure of real fluids from the simple fluid model,

$\omega_i$ is the acentric factor for component i.

The approximations for $\nu_i^{(0)}$ and $\nu_i^{(1)}$ are functions of the reduced temperature and reduced pressure for each component in the mixture. These approximations are empirical surface fits of the Curl and Pitzer correlation supplemented with some additional data covering the hypothetical regions.

The liquid phase activity coefficients are calculated from the Hildebrand[58] equation

$$\ln \gamma_i = V_i (\delta_i - \bar{\delta}_i)/RT \tag{4-7}$$

where: $V_i$ is the molal volume of the saturated liquid,

$\delta_i = \sqrt{\Delta E_v / V_i}$ the solubility parameter for component i,

$\bar{\delta}_i$ is the volume weighted average value of the solubility parameter for the mixture,

$E_v$ is the change in internal energy during the vaporization of component i.

The Hildebrand equation is only valid for regular solutions where interactions between different sized molecules are small and may be neglected. Fortunately, the paraffin hydrocarbons approximate regular solutions over a considerable range of temperature, pressure and composition.

Vapor phase fugacity coefficients may be calculated from volumetric data or an equation of state by the thermodynamic relation

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left( \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right) dV - RT \ln Z \tag{4-8}$$

where:   V is the total volume of the vapor mixture,

Z is the compressibility factor for the mixture at system conditions.

Chao and Seader used the two constant Redlich-Kwong[59] equation to evaluate the derivative in Equation 4-8.  The mixing rules for the Redlich-Kwong equation are simply

$$a = \Sigma \ y_i \ a_i \qquad\qquad (4-9)$$

$$b = \Sigma \ y_i \ b_i \qquad\qquad (4-10)$$

where:   $a_i$, $b_i$ are the Redlich-Kwong constants which can be evaluated from the critical properties of each component.

When Equation 4-8 is evaluated using the Redlich-Kwong equation of state and the mixing rules of Equations 4-9 and 4-10, Chao and Seader have shown that

$$\ln \ \phi_i = (Z - 1)b_i/b - \ln(Z - bP)$$
$$- a^2/b \left(2a_i/a - b_i/b\right) \ln(1 + bP/Z) \qquad (4-11)$$

It is important to note that this relatively simple expression for $\phi_i$ is due to the simplicity of both the Redlich-Kwong equation of state and the mixing rules of Equations 4-9 and 4-10.  The mixing rules establish the compositional dependence for the derivative in Equation 4-8.  To be totally consistent with the development of the Chao-Seader correlation, the mixture Z in Equation 4-11 should be evaluated from the Redlich-Kwong equation.  In practice, however, the Z can be calculated from a generalized corresponding states correlation.

The Chao-Seader correlation is generally applicable only for pressures below 2000 psia and therefore, is seldom used

for reservoir engineering calculations. The pressure limita-
tion results from a restriction on the correlation that the
pseudoreduced temperature of the liquid phase be less than
about 0.93. The solubility of methane in the liquid increases
with pressure to the point where this temperature restriction
causes the correlation to breakdown.

Another difficulty with the Chao-Seader correlation is
the failure of the Hildebrand equation to correctly predict
methane behavior in the liquid mixture. Differences between
experimental and calculated K-values for methane are system-
atic and Besserer[60] has shown that correction factors for
methane K-values can be correlated with the critical temper-
ature and critical pressure of the mixture. Figure 4-3 shows
the correction factors for three methane binaries at 100°F.
Application of these correction factors extends the pres-
sure range of the Chao-Seader correlation, however, even
with this correction the method is of limited use for reser-
voir engineering calculations. The next section outlines a
calculation procedure which avoids this pressure limitation.

## 4.5  Combined Chao-Seader and Critical Composition Methods

The critical composition method provides a rigorous
procedure for calculating the pressure at the point where
the K-values on a plot of log $K_i$ versus log P converge to
unity. Thus, the possibility exists for calculating K-values
over the full range of pressure by using the Chao-Seader
method to generate a number of K-values for each component
at the lower pressures and extrapolating these to the
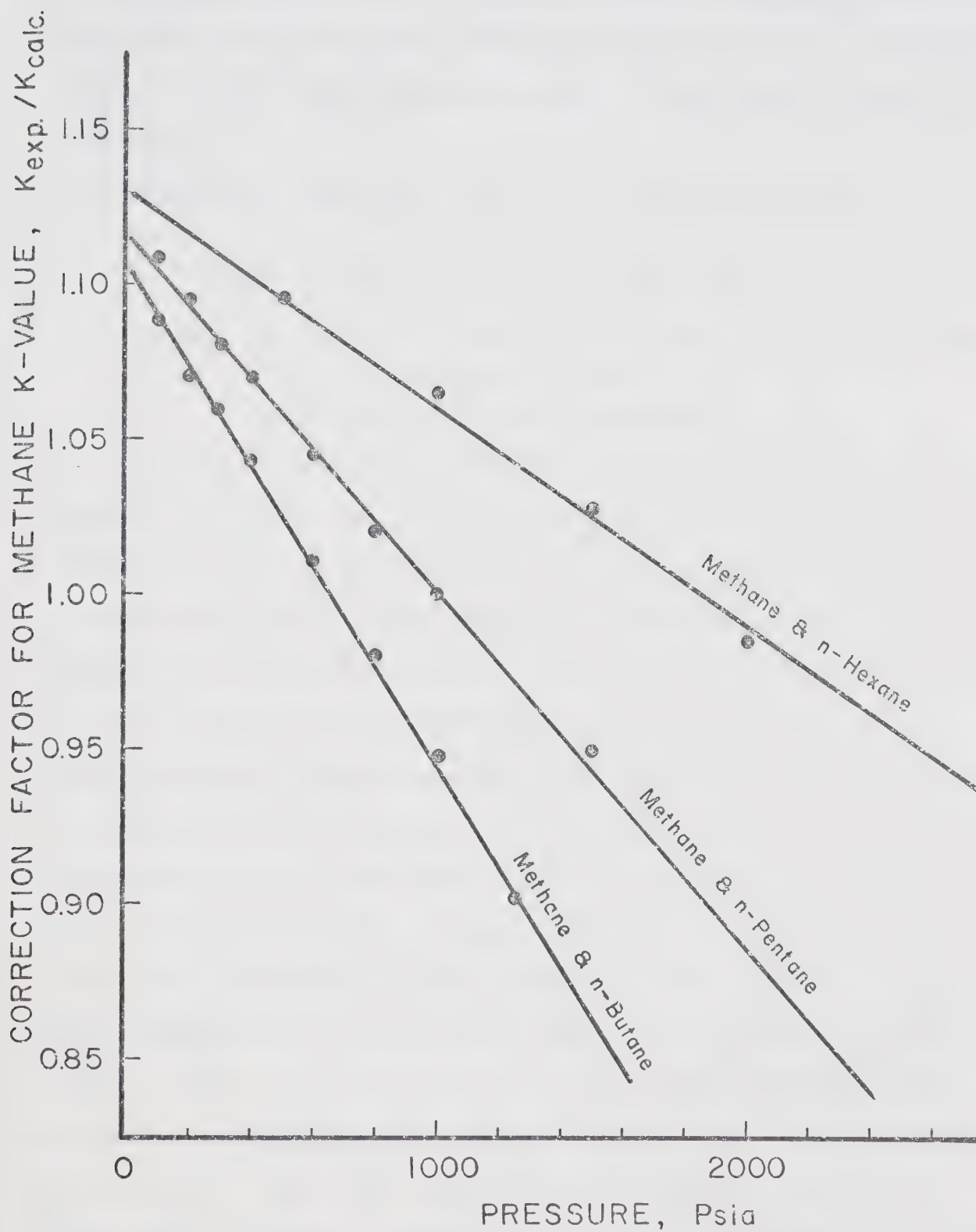
Figure 4-3. Correction Factors for Methane K-values from the Chao-Seader Correlation at 100°F.

convergence pressure given by the critical composition method. All that is required is a functional form which will suitably approximate the characteristic shape of the log $K_i$ versus log P diagram.

Green and Hachmuth[28] used the empirical equation

$$K_i = C_{1i}(1 - P/P_k)^n + C_{2i}/P + C_{3i}P^2 + C_{4i} \qquad (4\text{-}12)$$

where: $C_{1i}$, $C_{2i}$, $C_{3i}$ and $C_{4i}$ are empirical coefficients,
P is the system pressure,
$P_k$ is the convergence pressure.

to correlate K-values for binary mixtures of paraffin hydro-carbons. The four coefficients were required to satisfy the conditions that $K_i$ be unity at the vapor pressure and at the convergence pressure, and that $K_i$ of the least volatile component pass through a minimum. The characteristic shape of a log $K_i$ versus log P diagram for the more volatile compo-nents could be described with fewer coefficients, however, the same equation was used for all components. Green and Hachmuth tried various values for the exponent n and found that 0.25 gave the best average fit for binary mixtures of the normal paraffins. They correlated the four coefficients directly with the system composition and the physical prop-erties of the pure components. In this work Equation 4-12 was only required to extrapolate K-values into the high pres-sure region. When the calculated convergence pressure was less than 3000 psia, the four coefficients in Equation 4-12 were calculated using the convergence pressure and K-values from the Chao-Seader correlation for pressures of 0.3 $P_k$,

0.5 $P_k$ and 0.7 $P_k$. When the convergence pressure was greater than 3000 psia, K-values corresponding to 0.1 $P_k$, 0.3 $P_k$ and 0.5 $P_k$ were used. After the four coefficients in Equation 4-12 were calculated for every component in the mixture it was possible to perform flash calculations throughout the high pressure region. A FORTRAN computer program for this calculation procedure is given in Appendix D.

Chapter 5.   CALCULATION OF VAPOR AND LIQUID DENSITIES

## 5.1  Foreword

Computer programs for modelling the performance of petro-
leum reservoirs require a method for calculating fluid densi-
ties.  This may be accomplished with a corresponding states
correlation extended to mixtures through the use of the con-
cept of pseudocritical properties.

In order to use corresponding states correlations, a
suitable method must be found to adapt the information to
computer use.  This may involve interpolation techniques,
fitting empirical functions to all or part of the data, or
by using a reduced form of an equation of state.  Interpola-
tion techniques are considered the least desirable, because
large-scale data storage and subsequent retrieval is an in-
efficient computer operation.  The well-known equations of
Beattie and Bridgeman[61], and Benedict, Webb and Rubin[62],
have been applied in reduced form to generalized correlations
by Su and Chang[63], Opfell, Sage and Pitzer[64], and Su and
Viswanath[65].

Good accuracy has been achieved using these equations
in the gaseous region, but unfortunately it has not been pos-
sible to find a single set of coefficients that will give
good results over the entire liquid, gaseous and saturated
regions.  Hirschfelder, Buehler, McGee and Sutton[66] have
developed a generalized equation of state in which different
functions are used for the three regions defined as:  (1) gas,
where the reduced density is less than one; (2) dense gas,

where the reduced density is greater than one and the reduced
temperature is greater than one; and (3) liquid, where the
reduced density is greater than one and the reduced tempera-
ture is less than one. The functions increase in complexity
for each of the three regions. The equations are density im-
plicit, and a method for obtaining a solution when the re-
duced temperature and pressure are known was not reported.
Yen and Woods[67] have developed accurate empirical expressions
for the saturated and compressed liquid regions when the re-
duced tempeature is less than one for the Lydersen, Green-
korn and Hougen[31] correlation. The expressions in their
computer-oriented approach have the advantage of being den-
sity explicit, however, the equations are lengthy and more
than 80 coefficients are required.

On the basis of these considerations, it was concluded
that no generally applicable equation of state was available
for representing fluid densities from generalized correla-
tions. Futhermore, it appeared that previous attempts to
develop equations of state for pure materials had not given
sufficient recognition to the behavior of the reduced iso-
chores, particularly along the saturation curve, when se-
lecting the independent variable.

## 5.2 Some Equation of State Features

One of the most informative projections of PVT data is
the isochoric plot shown on reduced coordinates in Figure
5-1. If all pure substances conformed to van der Waals' two-
parameter theorem of corresponding states, all PVT data
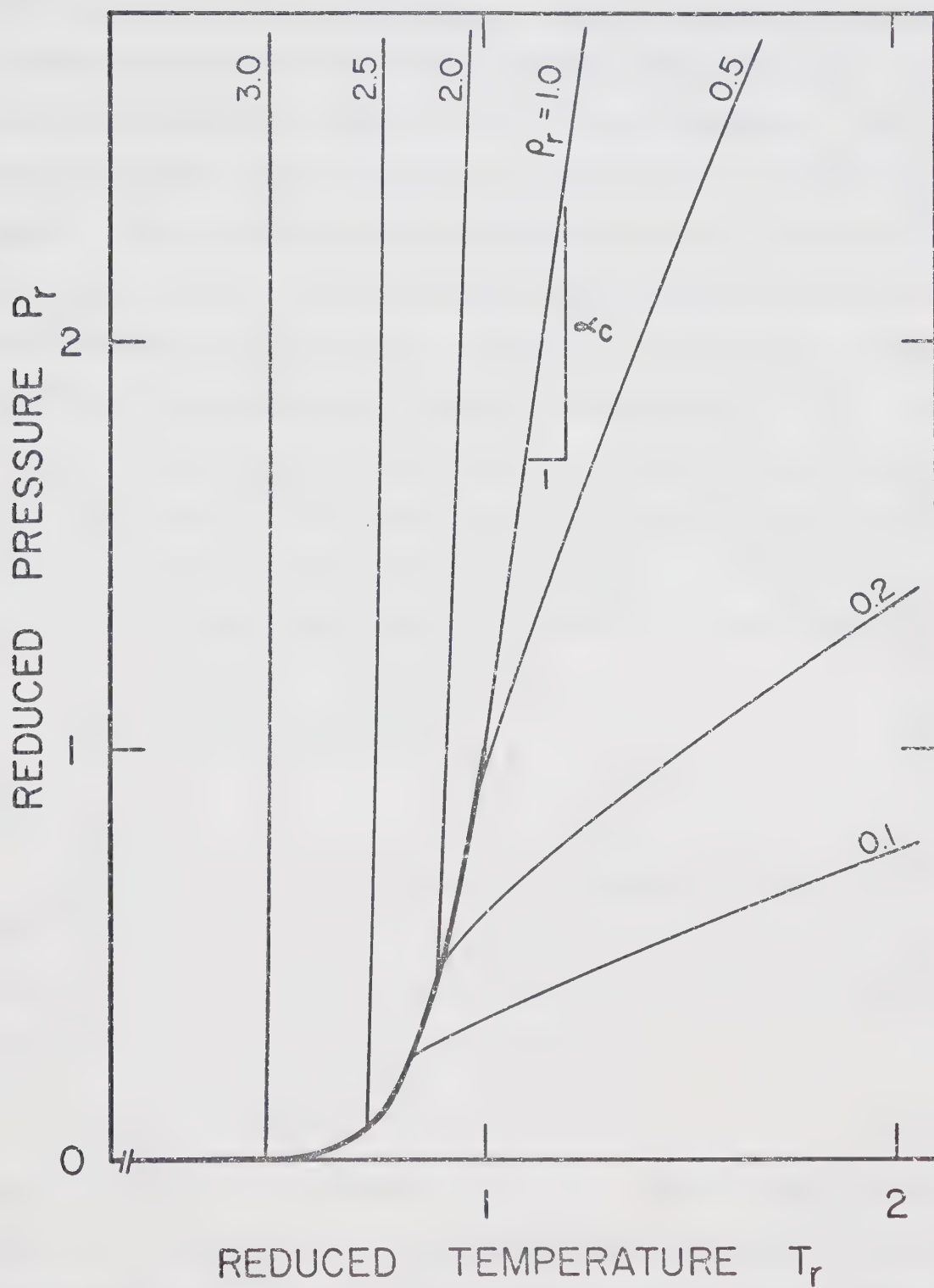
Figure 5-1.  Isochoric Diagram Showing The Vapor Pressure Curve.

would lie on a single plot. In actual fact, however, the re-
duced critical point is the only point which is assured of
being common for all substances. Various methods have been
proposed to resolve the problem of departure from the two-
parameter theorem by introducing a third parameter. For ex-
ample, the acentric factor, $\omega$, introduced by Pitzer[68] repre-
sents a method of describing the departure of a substance
from the intermolecular potential function for a simple fluid
with spherical molecules by observing the variation in re-
duced vapor pressure at a reduced temperature of 0.7. Riedel
[69] developed a comprehensive corresponding states method by
using the slope of the vapor pressure curve at the critical
point as a third parameter. He defined $\alpha_c$ as the logarith-
mic slope of the vapor pressure curve at the critical point

$$\alpha_c = \frac{d(\ln P_r)}{d(\ln T_r)} = \frac{T_r}{P_r}\frac{dP_r}{dT_r} \tag{5-1}$$

where $T_r = 1$.

Experimental evidence generally supports the observation
from Figure 5-1 that the critical isochore is linear with a
slope which is continuous with and equal to that of the vapor
pressure curve. Hence one can write

$$\left(P_r\right)_{\rho_c} = 1 + \alpha_c(T_r - 1) \tag{5-2}$$

along the critical isochore, $\rho_c$. It is significant to note
that the origin of both the parameters $\omega$ and $\alpha_c$ may be traced
directly to the behavior of the substance along the vapor
pressure curve. It may be concluded from this that the be-
havior of the substance along the vapor pressure curve

represents one of the major obstacles to developing an equation of state that is applicable to both the gaseous and liquid-like regions.

The isochores for a pure component are also linear in the region of very low density and in the region of high reduced temperature. The approximate linearity of the isochores has been used in developing most empirical equations of state. Beattie and Bridgeman[61] and Benedict, Webb and Rubin[62] used the form

$$(P_r)_{\rho_r} = A + B \, T_r + C \, T_r^{-2} \tag{5-3}$$

to describe the isochores. The term $CT_r^{-2}$ diminishes with increasing temperature and satisfies the condition that the isochores become linear at high temperature. Martin and Hou[70] used the expression

$$(P_r)_{\rho_r} = A + B \, T_r + C \, \exp(-k \, T_r) \tag{5-4}$$

where k was found to be a universal constant.

The coefficients A, B and C in Equations 5-3 and 5-4 are functions of density. These equations can be applied to a range of densities if it is assumed that their functional dependence on density can be approximated by a power polynomial of degree n, namely

$$P_r = \sum_{i=1}^{n} \left( A_i + B_i T_r + C_i T_r^{-2} \right) \rho_r^{\ i} \tag{5-5}$$

and

$$P_r = \sum_{i=1}^{n} \left( A_i + B_i T_r + C_i \exp(-k \, T_r) \right) \rho_r^{\ i} \tag{5-6}$$

Some of the coefficients $A_i$, $B_i$ and $C_i$ may be evaluated

by imposing certain known limiting physical conditions such
as:

(i) the substance must exhibit ideal gas behavior as the
pressure approaches zero so that $P_r Z_c/(\rho_r T_r) = 1.0$ as $P_r \to 0$
for all $T_r$;

(ii) the slope of the critical isotherm is zero at the
critical point so that $(\partial P_r/\partial \rho_r)_{T_r=1} = 0$;

(iii) a point of inflection in the critical isotherm must
exist at the critical point so that $(\partial^2 P_r/\partial \rho_r^2)_{T_r=1} = 0$.

The remaining coefficients are usually obtained by
applying a least squares criterion to minimize the deviation
between the predicted and observed pressures, or preferably
the deviation between the predicted and observed densities[71,
72].

Equations 5-5 and 5-6 have the form of a truncated viral
expansion. Thus, the assumption that the dependence of $A_i$,
$B_i$ and $C_i$ on density could be approximated by a polynomial in
density is tantamount to assuming that the temperature de-
pendence of the second and higher virial coefficients can be
represented by the same functional form as that of Equations
5-3 and 5-4. As these equations were intended to represent
isochores, and not necessarily the temperature dependence of
the virial coefficients, it is not surprising that Equations
5-5 and 5-6 fail at high densities.

The curvature of the isochores on a pressure-temperature
diagram changes from concave downward to concave upward in
passing through the critical density. At extremely high den-
sities there is some evidence that the isochores straighten

and become concave downward. Thus, the coefficient $\sum_{i=1}^{n} C_i \rho_r^i$ in Equations 5-5 and 5-6 should change sign when crossing the critical density. This is one of the constraints implied by Equation 5-2. The additional constraints implied by Equation 5-2, namely that when $\rho_r = 1$, $\sum_{i=1}^{n} A_i = 1 - \alpha_c$ and $\sum_{i=1}^{n} B_i = \alpha_c$, are not normally used in equation of state development.

When the physical behavior of a system is not fully used in determining the form of, or the coefficients for an equation of state, one always faces the possibility of encountering correlated coefficients. Correlation of coefficients in approximating functions often occurs when variables are employed in an inappropriate form, or when improper variables are used. Correlation of coefficients is not desirable inasmuch as the coefficients become sensitive to the data set from which they were obtained. An improper functional form also prevents extrapolation outside the range of conditions for which data were available. Unfortunately, the coefficients in most equations of state tend to be correlated.

Consider, for example, the vapor pressure curve which is most conveniently described by a relationship between the variables $\log P_r$ and $T_r^{-1}$. As most equations of state do not employ the variables $P_r$ and $T_r$ in this form at saturation, a complicated interdependence among all coefficients is required if the vapor pressure is to be accurately predicted. Consider also the coefficient $\sum_{i=1}^{n} A_i \rho_r^i$, which may be thought of as an intercept or origin for the line approximating an isochore. Isochores have their origin at the

saturated state, and any other origin is an extrapolation into a hypothetical region. A computational scheme has been developed in this work which uses a vapor pressure equation at saturation, and eliminates the need for $A_i$ coefficients to describe isochores.

The isochores of Figure 5-1 depict the derivative $(\partial P_r/\partial T_r)_{\rho_r}$. Figure 5-2 is also an isochoric diagram which has the advantage of showing the two phase envelope. The transformation relating Figure 5-1 to Figure 5-2 can be obtained by making the substitution

$$P_r = \rho_r Z T_r / Z_c \tag{5-7}$$

in the derivative with the result that

$$\left(\partial P_r/\partial T_r\right)_{\rho_r} = \rho_r/Z_c \left(\partial (Z T_r)/\partial T_r\right)_{\rho_r} \tag{5-8}$$

Hence, recalling the definition given in Equation 5-1, it may be shown that the slope of the critical isochore is $Z_c \alpha_c$ on this diagram. The isochores of Figure 5-2 become linear at low densities, and exhibit a slope of one as the limiting condition of zero density is approached.

If Equation 5-7 is solved for $T_r$, and the substitution made in the derivative $\left(\partial T_r/\partial P_r\right)_{\rho_r}$, then

$$\left(\partial T_r/\partial P_r\right)_{\rho_r} = Z_c/\rho_r \left(\partial (P_r/Z)/\partial P_r\right)_{\rho_r} \tag{5-9}$$

and the pressure isochoric diagram illustrated in Figure 5-3 is obtained. On this diagram the critical isochore has a slope of $(Z_c \alpha_c)^{-1}$ and the low-density isochores again exhibit a limiting slope of one.
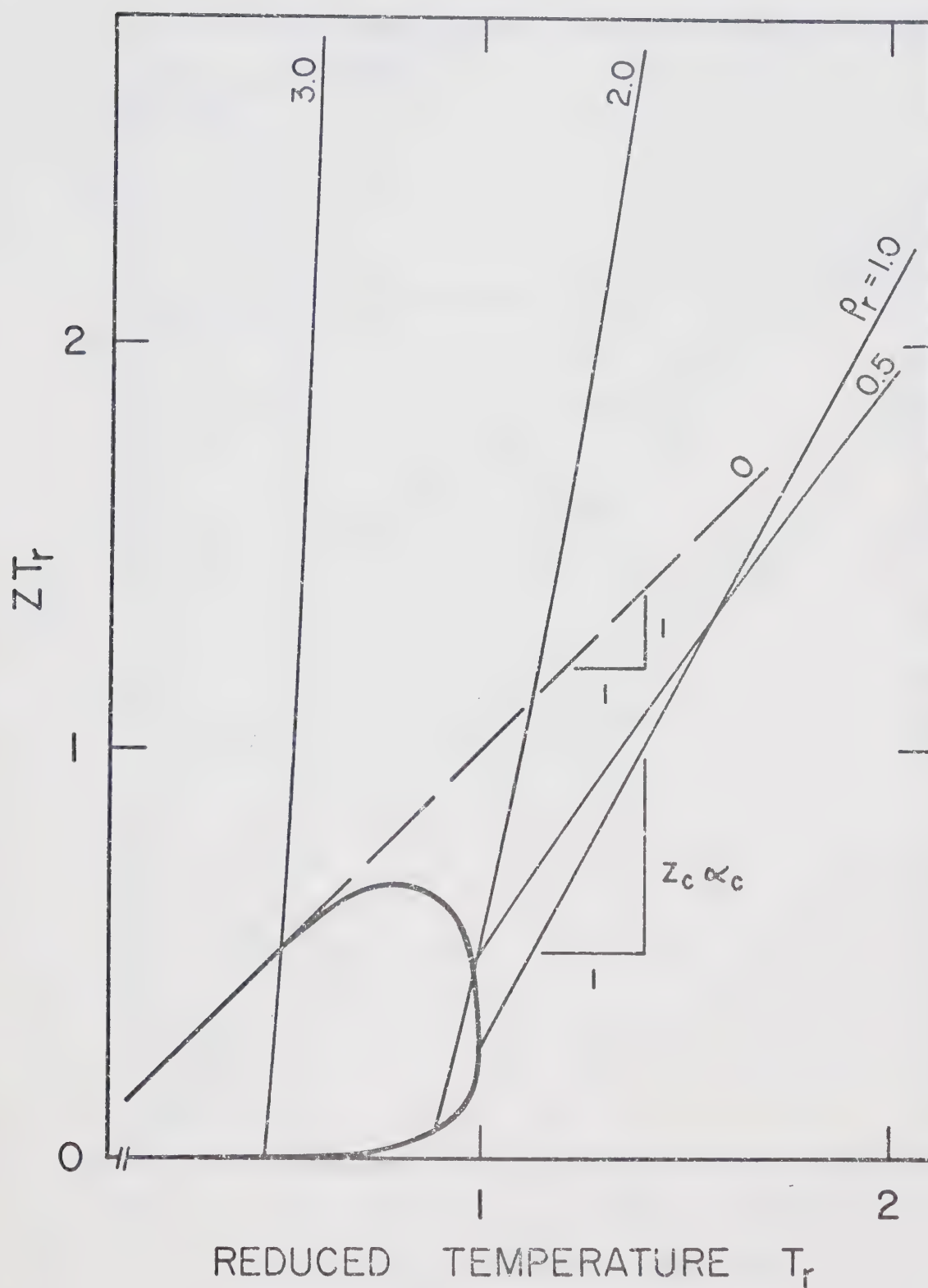
Figure 5-2.  Temperature Isochoric Diagram Showing the
             Two-Phase Envelope.
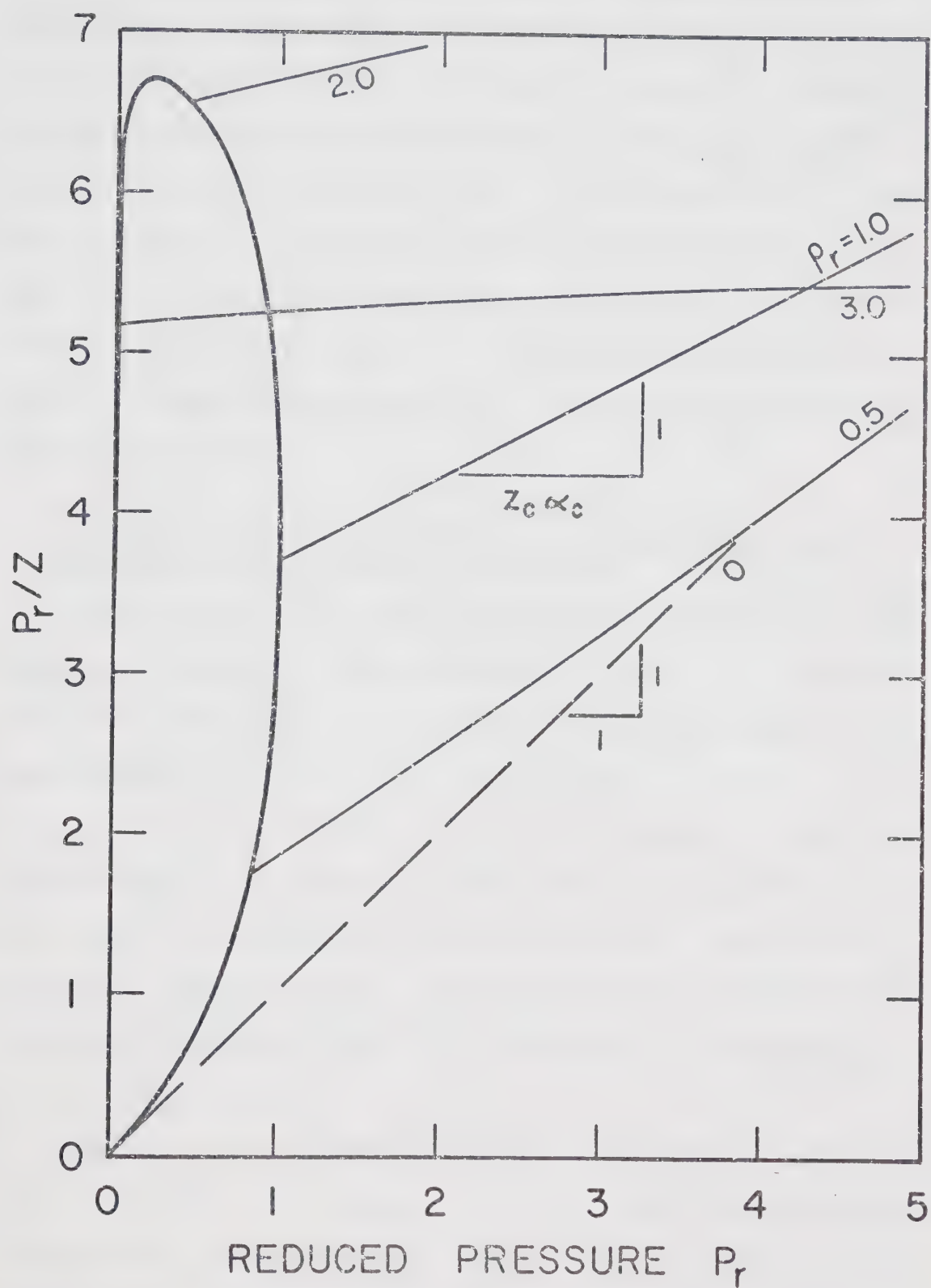
Figure 5-3.  Pressure Isochoric Diagram Showing the
Two-Phase Envelope.

By taking the saturated state as a datum, as suggested previously, the isochores of Figures 5-2 and 5-3 can be drawn from a common origin as shown in Figure 5-4. Because the isochores in Figure 5-4 all pass through the origin, an intercept term will not be required in any approximating expressions used to represent them. It should also be noted that the slopes of the isochores in Figure 5-3 are the reciprocals of those in Figure 5-2. This reciprocal feature is more apparent in Figure 5-4 and can be used to develop either a temperature-explicit or a pressure-explicit form for the isochores.

## 5.3 A General Method for Analytical Representation of Compressibility Factor Correlations

A procedure which uses independent equations for the saturated region and the isochores of Figure 5-4 has been developed. The use of independent equations results in the density-implicit forms $\rho_r = f(Z_c, \alpha_c, \rho_r, T_r)$ and $\rho_r = g(Z_c, \alpha_c, \rho_r, P_r)$ for the isochores of Figures 5-2 and 5-3, respectively. In principle these forms can be solved by any of the well-known iterative techniques. However, to guarantee convergence and retain simplicity, the method of interval halving was used. The procedure is outlined in the following steps:

1. Given $Z_c$, $\alpha_c$, $P_r$ and $T_r$, two initial values of density $\rho_r^{(1)}$ and $\rho_r^{(2)}$, are required such that the two corresponding values of the function $F(\rho_r) = \rho_r - f(Z_c, \alpha_c, \rho_r, P_r)$ have opposite sign. A choice of $\rho_r^{(1)} = 0$, results in $F(\rho_r^{(1)}) = -P_r Z_c/T_c$, because $Z = 1.0$ at zero density. A choice of

85
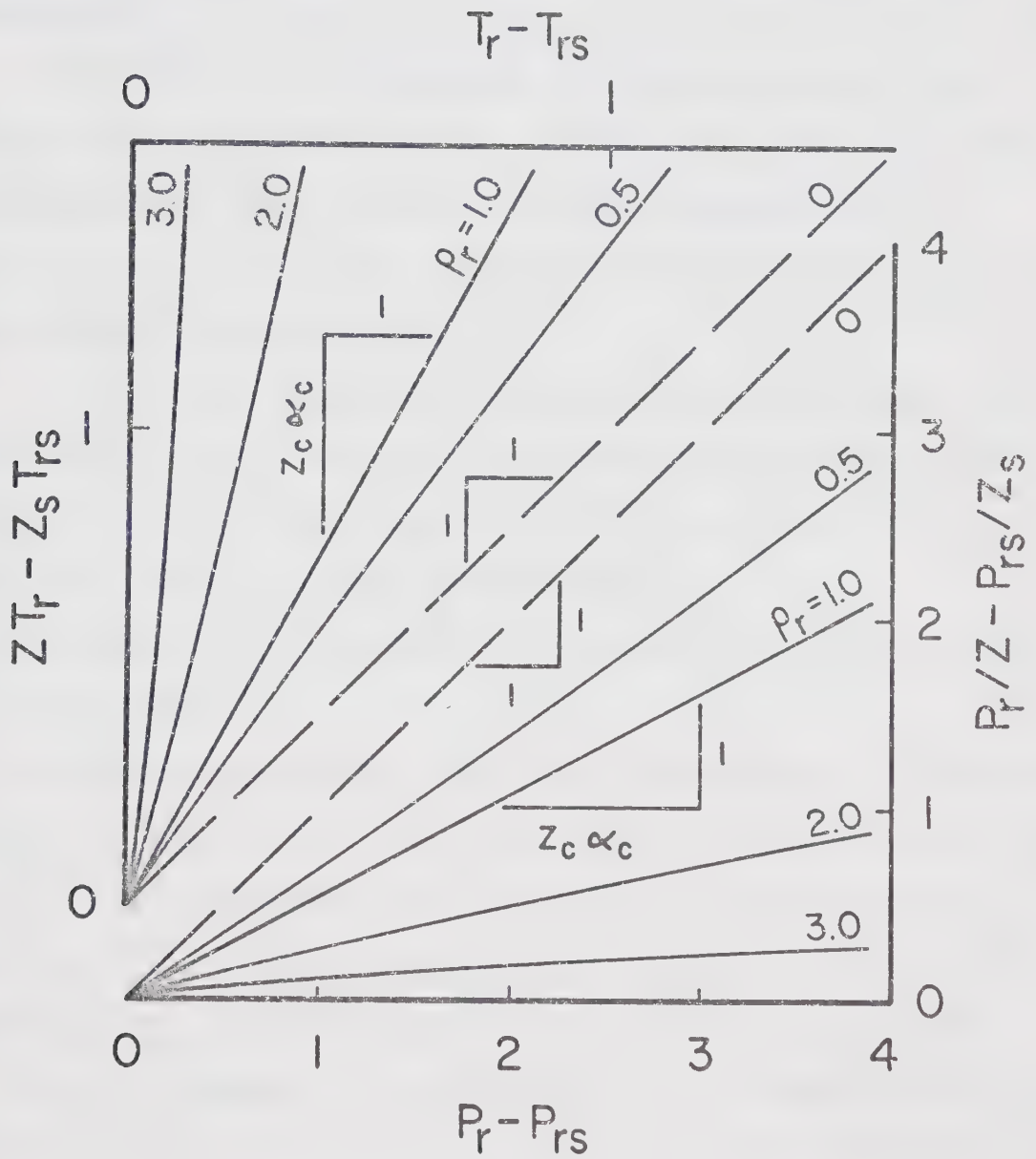


Figure 5-4.   Isochoric Diagrams with the Saturated State
             Taken as a Datum.

$\rho_r^{(2)}$ equal to the highest density covered by the correlation will yield a positive value for $F(\rho_r^{(2)})$ if the solution lies in the range of the correlation.

2. An improved estimate of density, $\rho_r^{(3)}$, is calculated, and for the method of interval halving it is simply the average of $\rho_r^{(1)}$ and $\rho_r^{(2)}$, i.e. $\rho_r^{(3)} = (\rho_r^{(1)} + \rho_r^{(2)})/2$.

3. If $\rho_r^{(3)} > 1.0$, an equation for the saturated liquid region of the general form $\rho_{rs} = f(T_{rs})$ is solved for the temperature of the saturated liquid corresponding to $\rho_r^{(3)}$ from step 2. If $\rho_r^{(3)} < 1.0$, an equation for the saturated vapor region is solved for $T_{rs}$.

4. The vapor pressure corresponding to $T_{rs}$ from step 3 is calculated from a vapor pressure equation for the substance or from a generalized vapor pressure equation with a parameter which characterizes the substance.

5. Equation 5-7 is applied to the saturated state and $P_{rs}/Z_s$ is calculated.

6. An expression for the isochores of Figure 5-4 of the form $(P_r/Z - P_{rs}/Z_s) = f(Z_c, \alpha_c, \rho_r, P_r-P_{rs})$ is solved for Z, and $F(\rho_r^{(3)})$ is calculated. If $F(\rho_r^{(3)}) < 0$, the values of $\rho_r^{(1)}$ and $F(\rho_r^{(1)})$ in step 2 are replaced with $\rho_r^{(3)}$ and $F(\rho_r^{(3)})$, respectively, otherwise $\rho_r^{(2)}$ and $F(\rho_r^{(2)})$ are replaced.

7. Steps 2 through 6 are repeated until a convergence criterion, such as $|\rho_r^{(1)} - \rho_r^{(2)}|/\rho_r^{(1)} < \varepsilon$, is satisfied where $\varepsilon$ is some arbitrarily small value.

To utilize the above procedure, the following relationships are required:

(i) an equation relating the density of the saturated liquid

to the saturation temperature;

(ii) a vapor pressure equation;

(iii) an equation relating the density of the saturated vapor to the saturation temperature;

(iv) an expression for the $P_r/Z$ isochores illustrated in Figure 5-4.

Now that the theory and general procedure have been developed, the method will be demonstrated using a published corresponding states correlation as a data source.

## 5.4 Application of the Generalized Equation of State Method to the Lydersen et al. Correlation

The Lydersen, Greenkorn and Hougen[31] correlation was selected as a data source because it presents data covering a wide range of densities with reduced temperatures from 0.3 to 15, and reduced pressures from saturation to 30. The correlation uses the critical compressibility factor as a third parameter, and tabular data are provided for $Z_c$ values of 0.25, 0.27 and 0.29. The four relationships required to apply the generalized equation of state method to this correlation are discussed in the following sections.

## 5.4 (a) Saturated Liquid Densities

The two-phase region for a pure substance is specified by a single intensive variable. Most saturated liquid equations are explicit in density with either $T_{rs}$ or $P_{rs}$ as the independent variable. Since $T_{rs}$ must be evaluated in every iteration of the solution procedure, an equation which is explicit in temperature would be preferable. Several equations for the saturated liquid state can be developed from

Taylor expansions about the critical point. A comprehensive discussion of Taylor expansions, the "law of rectilinear diameters"

$$\rho_{rL} + \rho_{rV} = 2 + D(1 - T_{rs}) \tag{5-10}$$

and the cubic coexistence curve

$$\rho_{rL} - \rho_{rV} = E(1 - T_{rs})^{1/3} \tag{5-11}$$

are given by Davis and Rice[73]. Their tabulated values of D and E for various substances suggests that the form

$$\rho_{rL} = 1 + (D_1 + D_2 Z_c)(1 - T_{rs})$$
$$+ (E_1/Z_c)(1 - T_{rs})^{1/3} \tag{5-12}$$

might be appropriate for representing the saturated liquid data of the Lydersen et al. correlation. When the coeffic- ients $D_1$, $D_2$ and $E_1$ were evaluated using a least-squares criterion, the average deviation from the data source was 0.78 per cent, indicating the forms to have some merit.

Rackett[74] recently reported the simple but accurate equation

$$\rho_{rL}^{-1} = Z_c (1 - T_{rs})^{2/7} \tag{5-13}$$

This equation gave results differing from the data source by an average of 0.66, 0.37 and 1.31 per cent for $Z_c$ values of 0.25, 0.27 and 0.29, respectively. Rackett stated that a relation between $Z_c$ and the exponent 2/7 is not detectable from experimental evidence. However, to force a better correspondence with the data source, the modified form

$$\rho_{rL}^{-1} = (0.193 + 3.789 Z_c^3)(1 - T_{rs})^{(0.220 + 3.52 Z_c^3)} \tag{5-14}$$

was developed. Equation 5-14 differs from the data source by an average of 0.08, 0.14 and 0.23 per cent for the three respective $Z_c$ values. It may be noted that Equations 5-13 and 5-14 have a computational advantage when used in the proposed iterative method because $T_{rs}$ can be calculated explicitly after taking the logarithm of both sides and solving for $T_{rs}$.

It was also demonstrated by Rackett that the saturated liquid data of Lydersen et al. can be calculated from the following equation by Riedel[69]

$$\rho_{rL} = 1 + 0.85(1 - T_{rs}) + (1.93 + 0.2(\alpha_c - 7))(1 - T_{rs})^{1/3} \qquad (5-15)$$

The saturated liquid density tabulations of the data source for $Z_c$ values of 0.25, 0.27 and 0.29 can be calculated from Equation 5-15 with standard errors of 0.07, 0.05 and 0.11 per cent, respectively. The $\alpha_c$ values which give these minimum differences are 8.0264, 6.8827 and 5.7045 for the respective $Z_c$ values. Since Equation 5-15 gave the best agreement with the data source, it was selected to describe the saturated liquid state.

5.4 (b) Vapor Pressure Equation

Because $\alpha_c$ is required in Equation 5-15 for the saturated liquid, and it will also be required for the slope of the critical isochore, it seems appropriate to use $\alpha_c$ for the vapor pressure calculation as well. Although $\alpha_c$ can be obtained from the definition expressed by Equation 5-1, it is usually obtained through application of Riedel's[69] generalized vapor pressure equation

$$\ln(P_r) = \alpha_c \ln(T_r) - 0.0838(\alpha_c - 3.75)$$

$$(36/T_r - 35 - T_r^6 + 42 \ln(T_r)) \qquad (5\text{-}16)$$

at a convenient temperature such as the normal boiling point. Hence, Equation 5-16 was used for vapor pressure calculations in this work. Reid and Sherwood[75] have reviewed this equation and report an average maximum error of 5.3 per cent for pressures less than 1500 mm of Hg; for pressures greater than 1500 mm of Hg, the average maximum error was 1.7 per cent.

The Lydersen et al. correlation used $Z_c$ rather than $\alpha_c$ as the third parameter, and consequently a relation between them is required. Riedel[69] reports the equation

$$\alpha_c = (Z_c^{-1} - 1.90)/0.26 \qquad (5\text{-}17)$$

which relates the two parameters within ± 2 per cent. However, the $\alpha_c$ values from Equation 5-17 for $Z_c$ values of 0.25, 0.27 and 0.29 do not agree with the ones which give the best correspondence between Equation 5-15 and the saturated liquid region of the data source. In order to be consistent, the same values of $\alpha_c$ given previously for use in Equation 5-15 were applied in Equation 5-16, and also in the expressions for the isochores.

## 5.4  (c) Saturated Vapor Densities

Attempts to solve for $\rho_{rV}$ from modified forms of Equations 5-10 and 5-11 invariably resulted in large relative errors for values of $T_{rs} < 0.9$. The same difficulty was reported by Bradford and Thodos[76]. These authors recommended using different equations for the temperature intervals $1.0 > T_{rs} \geqslant 0.9$ and $T_{rs} < 0.9$. They reported an average deviation

of 2.63 per cent between their equations and the experimental data for twelve hydrocarbons.

In the computational scheme previously outlined, any error in defining the saturated state is carried into the single-phase region. Unfortunately, all attempts to develop an accurate equation for the saturated vapor region of the data source have so far been unsuccessful.

In order to circumvent this difficulty, it was decided to try to use the gas branch of the critical isotherm as the reference condition rather than the saturated state which was used for $\rho_r > 1$. The saturated vapor curve and the critical isotherm coincide at the critical point. When the gaseous branch of the critical isotherm is used as a datum for the isochores, then the pressure difference $P_r - \left(P_r\right)_{T_r=1}$ gives the direction and magnitude of any departure from the critical isotherm along the isochores. If the pressure difference is negative, a test to see if $\left|P_r - P_{rs}\right| < \varepsilon$ may be used to check if the specified $T_r$ and $P_r$ are within some small $\varepsilon$ of the saturated vapor line.

Davis and Rice[73] derive the following equation for the gas branch of the critical isotherm

$$\left(P_r\right)_{T_r=1} = 1 - (5 - Z_c^{-1})(1 - \rho_r)^4$$
$$+ (4 - Z_c^{-1})(1 - \rho_r)^5 \qquad (5\text{-}18)$$

This equation gives pressures differing from the data source by standard errors of 0.77, 1.03 and 0.34 per cent, for $Z_c$ values of 0.25, 0.27 and 0.29, respectively. As Equation 5-18 gave better agreement with the data source than any of

the saturated vapor equations that were tried, it was used to calculate the datum for isochores when $\rho_r < 1$. There is also a computational advantage to Equation 5-18, because $\rho_r$ is an independent variable in the proposed iterative procedure, thereby permitting explicit calculation of $(P_r)_{T_r=1}$.

5.4 (d) Single-Phase Region - Isochores

Analytical functions to approximate the pressure iso-chores of Figure 5-4 should satisfy the following requirements. They should yield curves which:

(i) approach a limiting slope of one as $\rho_r \to 0$;

(ii) are concave upward for $0 < \rho_r < 1.0$;

(iii) become linear with a slope of $(Z_c \alpha_c)^{-1}$ when $\rho_r = 1.0$;

(iv) are concave downward for $\rho_r > 1.0$.

The functional form

$$\Delta(P_r/Z) = \Delta P_r \left(\frac{1}{Z_c \alpha_c}\right) \rho_r^{\left(G(\rho_r,\, Z_c \alpha_c) + H(\Delta P_r,\, Z_c \alpha_c)\right)} \quad (5-19)$$

where: $\Delta(P_r/Z) = P_r/Z - P_{rs}/Z_s$

and $\Delta P_r = P_r - P_{rs}$

satisfies these requirements. The function $G(\rho_r,\, Z_c \alpha_c)$ con-trols the initial slope of the isochores at departure from the two-phase region. The change in slope of the isochores in the single-phase region is controlled by the function $H(\Delta P_r,\, Z_c \alpha_c)$. Equation 5-19 gives a good approximation for the isochores with reduced densities greater than one, but is generally unsuitable for reduced densities less than one. For $\rho_r > 1.0$ it was found that for each of the three $Z_c$ values considered, the functions

$$G(\rho_r, \, Z_c\alpha_c) = G_1\rho_r^{1/2} + G_2\rho_r + G_3\rho_r^{3/2} \tag{5-20}$$

and

$$H(\Delta P_r, \, Z_c\alpha_c) = H_1(\Delta P_r)^{1/2} \tag{5-21}$$

give a satisfactory fit. The curvature coefficient, $H_1$, was found to be invariant with $Z_c\alpha_c$. It was also observed that a plot of $G(\rho_r, \, Z_c\alpha_c)$ versus $\rho_r$ for the three values of $Z_c$ results in three similar curves slightly displaced from each other by a distance approximately proportional to $(Z_c\alpha_c)^{-1}$. Thus, it was possible to make a cross-correlation with $Z_c$ by a single coefficient $G_4$, as follows:

$$G(\rho_r, \, Z_c\alpha_c) = \left(G_1\rho_r^{1/2} + G_2\rho_r + G_3\rho_r^{3/2}\right)$$
$$\left(1 + G_4\{(Z_c\alpha_c)^{-1} - 0.53812\}\right) \tag{5-22}$$

Equation 5-22 simplifies to Equation 5-20 for $Z_c = 0.27$ and $\alpha_c = 6.8827$, because the constant 0.53812 is the reciprocal of the product of these two parameters.

The non-linear least squares method proposed by Marquardt[77] was used to simultaneously calculate the following values of the coefficients in the functions $G(\rho_r, \, Z_c\alpha_c)$ and $H(\Delta P_r, \, Z_c\alpha_c)$ of Equation 5-19:

$G_1 = 5.07301$ $\qquad$ $G_2 = -5.37068$ $\qquad$ $G_3 = 1.66199$

$G_4 = 5.47736$ $\qquad$ $H_1 = 0.042744$

Table 5-1 makes a comparison of the fit obtained with these coefficients with respect to the 564 data points from which they were derived. Every point was given the same weighting, irrespective of its $Z_c$ value.

For the gaseous region, $0 < \rho_r < 1.0$, the slopes of the

TABLE 5-1

COMPARISON OF CALCULATED DENSITIES
WITH THE DATA SOURCE

| $\rho_r$ | $Z_c$ | No. of Points | $T_r$ Range | $P_r$ Range | Standard Error % | | |
|------|------|------|------|------|------|------|------|
| | | | | | Aver-age | Maxi-mum | Points > 1.0% |
| >1 | 0.25 | 155 | 0.3 to 1.0 | 0.1 to 30.0 | 0.53 | 1.87 | 14 |
| >1 | 0.27 | 254 | 0.3 to 3.0 | 0.1 to 30.0 | 0.77 | 3.53 | 38 |
| >1 | 0.29 | 155 | 0.3 to 1.0 | 0.1 to 30.0 | 0.55 | 3.02 | 11 |
| | | 564 | | | 0.65 | | |
| | | | | | | | Points > 2.0% |
| <1 | 0.25 | 104 | 1.0 to 2.0 | 0.1 to 1.15 | 2.40 | 18.31 | 16 |
| <1 | 0.27 | 157 | 1.0 to 2.0 | 0.1 to 7.00 | 2.20 | 6.93 | 43 |
| <1 | 0.29 | 104 | 1.0 to 2.0 | 0.1 to 1.15 | 2.03 | 15.20 | 15 |

isochores at departure from the two-phase region, or from the critical isotherm, were found to be a near linear function of density between the limiting values of one and $(Z_c \alpha_c)^{-1}$. However, the change in the slope of the isochores with $\Delta P_r$ was more difficult to determine and approximate. Some of the difficulty rests with the data source, inasmuch as the data for $T_r > 2$, corresponding to large $\Delta P_r$, were found to be rather scattered. Several functional forms were tried, but none were appreciably better than the following simple expression

$$\Delta(P_r/Z) = \frac{P_r - \left(P_r\right)_{T_r=1}}{1 + (Z_c \alpha_c - 1)\rho_r^{\{0.8 + 0.05(P_r - \left(P_r\right)_{T_r=1})\}}}$$

(5-23)

A comparison of Equation 5-23 with the data source is also presented in Table 5-1.

## 5.4 (e) Discussion

A pictorial comparison of the analytical functions and the data source is given for the case $Z_c = 0.27$ in Figure 5-5. A discrepancy with the data source occurs when the dots do not coincide with the intersections of the isotherms and isobars. Plotting PVT data on these coordinates represents a severe test of the data, because Z appears as the ordinate as well as in the denominator of the expression for the abscissa. Points from the data source for $T_r > 2$ were not plotted because they exhibited considerable scatter on this diagram.

An analogy between the compressibility factor diagrams associated with density-explicit and density-implicit formulations can be made. A conventional compressibility factor
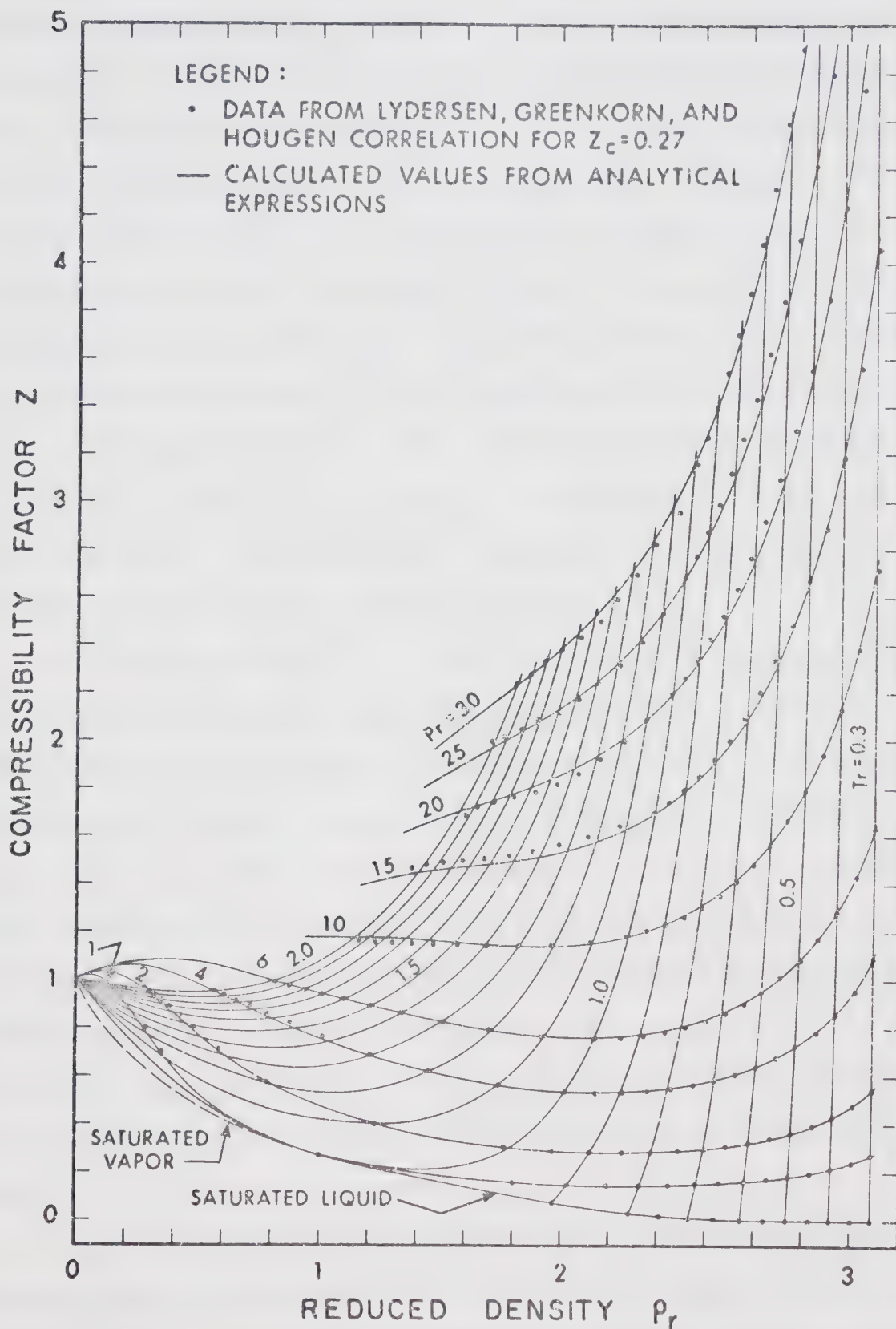
Figure 5-5. Compressibility Factor Diagram for the Lydersen, Greenkorn and Hougen Correlation.

diagram in which the dependent variable, Z, is the ordinate and the independent variables, $P_r$ and $T_r$, are abscissa and parameter, respectively, reflects a density-explicit formulation. The chart is used only once to read the Z factor corresponding to the values of the independent variables. The coordinates of Figure 5-5 correspond to a density-implicit formulation in which the chart is read at every trial while converging to the solution. An initial value of Z is assumed so that an estimate of the independent variable $\rho_r$ can be made using Equation 5-7. Then using independent variables of either $\rho_r$ and $P_r$ or $\rho_r$ and $T_r$, a new value of Z is read from the chart. Based on this value, a better estimate of density is made and the process repeated.

Reid and Sherwood[75], in reviewing various corresponding states methods for calculating liquid densities, found the Lydersen et al. correlation to compare favorably with other methods, and to have an accuracy of about 2 to 5 per cent. For densities greater than the critical, the present formulation approximates the correlation with a standard error of 0.65 per cent, and can therefore be considered an analytical representation of the tabular data. It is important to note that this standard error is with respect to the normal independent variables $P_r$ and $T_r$, as $\rho_r$ is always obtained from Equation 5-7.

For reduced densities less than one, the present functions should be considered as a qualitative representation of the tables. A satisfactory representation for this region hinges upon developing a suitable saturated vapor equation,

and either smoothing the data for $T_r$ > 2 or supplementing them with some additional data. The pressure range covered by the data source for $Z_c$ values of 0.25 and 0.29 is too small to permit development of a cross-correlation with $Z_c$.

## 5.4 (f) Conclusions

A general method for developing an equation of state for a pure substance has been presented. The method has a good theoretical basis, and is capable of representing a wide range of densities with a minimum number of constants. Application of the method to the raw data for various substances will assist in developing better equations for the isochores of Figure 5-4. It will also help to give a better understanding of the cross-correlations with $Z_c$ and $\alpha_c$.

The method illustrates the need for more than one correlating parameter in corresponding states treatments. The critical compressibility factor has been shown[31, 76] to be a good correlating parameter for the saturated vapor and liquid regions. It is also required to define the critical point. Riedel's factor is related to the slope of the isochores, and is fundamental to vapor pressure calculations using Equation 5-16.

Additional experience with the method, and the development of more accurate equations for the saturated vapor state will permit calculation of thermodynamic properties. In this connection the reciprocal feature illustrated in Figure 5-4, which shows the ability to express the isochores in their temperature-explicit or their pressure-explicit forms, will simplify the calculations.

A FORTRAN computer subroutine is given in Appendix C to solve the density-implicit form $f(Z_c, \alpha_c, \rho_r, P_r) = 0$ by the method outlined in the text. The subroutine is used to calculate the density of the liquid-phase in the computer program developed to simulate the depletion of a constant volume reservoir.

## 5.5 Application of Some Reduced Equations of State to the Standing and Katz Correlation

The compressibility factor chart of Brown and Holcomb[78] was revised and extended by Standing and Katz[30] based on the density data from sixteen saturated multicomponent gases and a comparison with pure methane data. The correlation is presented in chart form with independent variables of pseudo-reduced pressure and pseudo-reduced temperature. Pseudo-critical properties based on Kay's Rule[79] were used to calculate the pseudo-reduced pressure

$$
_p P_r = P / \sum_{i=1}^{n} y_i (P_c)_i \tag{5-24}
$$

and the pseudo-reduced temperature

$$
_p T_r = T / \sum_{i=1}^{n} y_i (T_c)_i \tag{5-25}
$$

The correlation only applies to the vapor phase since pseudo-critical properties are not suitable correlating parameters in the vicinity of the critical point. The lowest pseudo-reduced temperature covered by the correlation is 1.05.

The Standing and Katz correlation has received wide acceptance and usage by the petroleum industry. The correlation has also been used to evaluate several commonly used integrals

for calculating gas flows[80, 81]. Trube[82] used the correlation to prepare a chart for the pseudo-reduced coefficient of compressibility, $C_r$, defined as

$$C_r = P_r^{-1} - Z^{-1}\left(\partial Z/\partial P_r\right)_{T_r} \tag{5-26}$$

Trube noted that it was progressively more difficult to estimate the values of the derivative as the critical temperature was approached.

A tabular form[83] of the Standing and Katz correlation was used to calculate pseudo-reduced densities at regular intervals from the relation

$$\rho_r = 0.27\ P_r/(ZT_r) \tag{5-27}$$

The value of $Z_c = 0.27$ was arbitrary, but was considered representative of mixtures comprised chiefly of methane. Figure 5-6 is a plot of compressibility factor versus pseudo-reduced density and pseudo-reduced temperature. It should be noted that the isotherms for $T_r > 1.2$ plot as smooth curves, but that there are anomalous departures in the $T_r = 1.05$, 1.10 and 1.15 isotherms. These departures occur in the vicinity of the critical and may be due to experimental difficulties or more probably due to the failure of Kay's rule to correlate the data. Whatever the cause of the anomalies, it is apparent that a reduced form of an equation of state could not be expected to satisfactorily represent these isotherms. Hence, smooth and continuous curves were drawn for these isotherms and smoothed values obtained for analytical representation of the correlation.

The Benedict, Webb and Rubin[62] (B-W-R) equation of
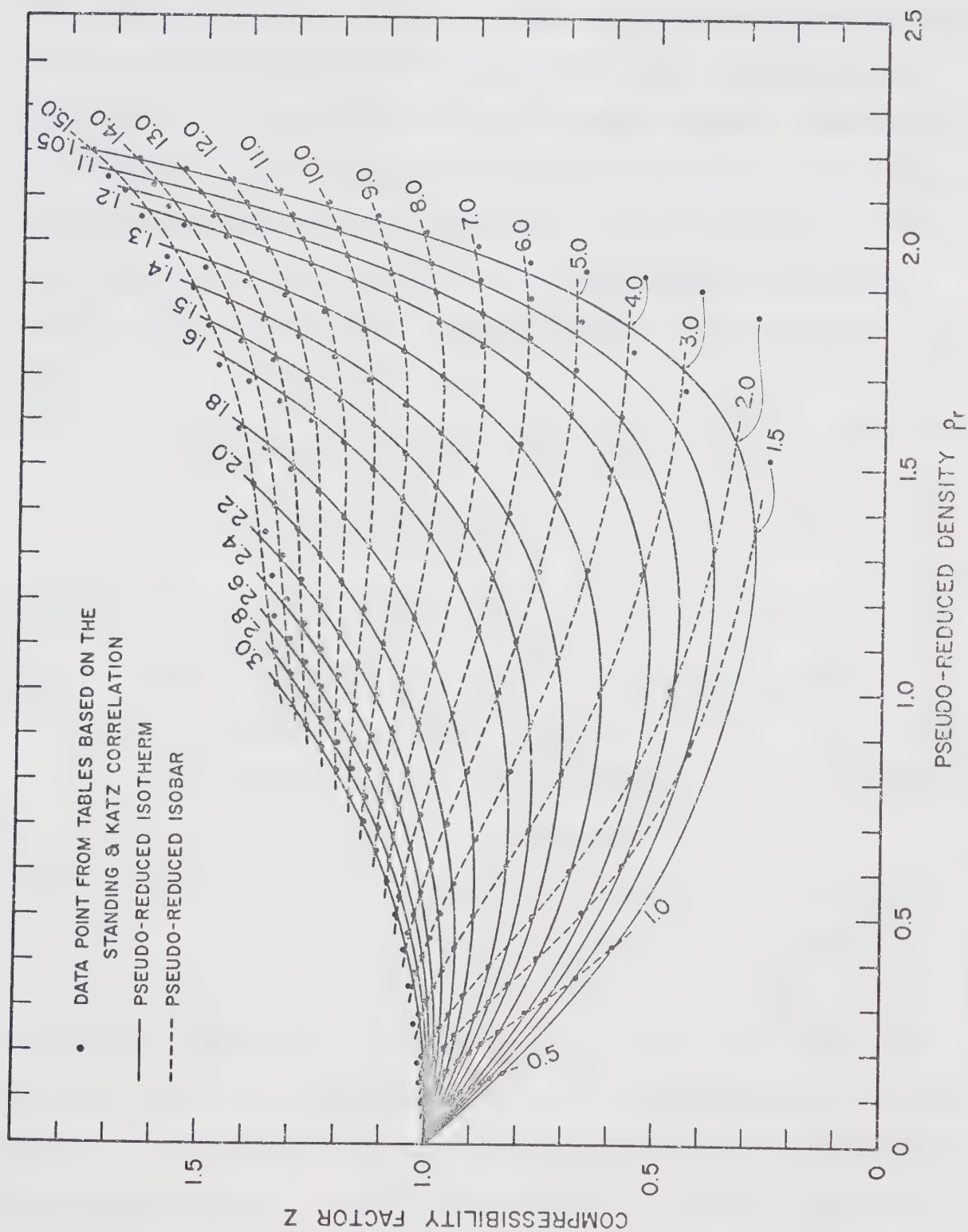
Figure 5-6. Compressibility Factor Diagram for the Standing and Katz Correlation.

state has been widely used to correlate the volumetric and thermodynamic properties of pure materials. Benedict et al. also proposed mixing rules for the eight coefficients in the equation so that it could be applied to gas mixtures. To apply the B-W-R equation to the Standing and Katz correlation the tabular data of reference 83 were treated as though they were reduced experimental data for a pure component. Since the correlation is in terms of the compressibility factor, the following form of the B-W-R equation was used to fit the data

$$Z = 1 + \left(A_1 + A_2/T_r + A_3/T_r^3\right)\rho_r + \left(A_4 + A_5/T_r\right)\rho_r^2$$
$$+ A_5 A_6 \rho_r^5/T_r + A_7 \rho_r^2/T_r^3 \left(1 + A_8 \rho_r^2\right)\exp\left(-A_8\rho_r^2\right)$$

$$(5-28)$$

The non-linear least squares method of Marquardt[77] was used to calculate the following values of the coefficients

$A_1 = 0.31506237$     $A_2 = -1.0467099$     $A_3 = -0.57832727$

$A_4 = 0.53530771$     $A_5 = -0.61232032$     $A_6 = -0.10488813$

$A_7 = 0.68157001$     $A_8 = 0.68446549$

These coefficients were obtained by minimizing the relative error in Z. When the independent variables are $\rho_r$ and $T_r$ the standard error in Z is 0.0101, or 0.87 per cent. When the normal independent variables of $P_r$ and $T_r$ are used with Equation 5-27 the standard error in Z is 0.00445, or 0.54 per cent with respect to the 1500 data points used to determine the coefficients. As with any equation of state, the region in the vicinity of the critical point is subject to the largest errors. The largest deviation was 7.15 per cent at the

point $T_r = 1.05$ and $P_r = 1.30$. There were six other points
in this region where the correlation and the B-W-R approxima-
tion differed by more than two per cent. Since Trube[82] had
difficulty evaluating the pseudo-reduced coefficient of
compressibility in this region it is likely that some of the
discrepancies are inherent in the correlation. The Standing
and Katz correlation was compared with some data not used in
its development and was found to be accurate within 1.2 per
cent[84]. Thus, except for a small region along the $T_r = 1.05$
and 1.10 isotherms the B-W-R approximation gives an acceptable
analytical representation of the correlation. A FORTRAN sub-
routine called ZKATZ is given in Appendix C for calculating
vapor phase densities using Equations 5-27 and 5-28.

An attempt was made to improve the analytical represen-
tation in the region of the critical point. The approach
used was based on the temperature isochoric diagram illustrat-
ed in Figure 5-2. The diagram suggests that any isotherm can
be used as a datum for the isochores. Since the $T_r = 1.05$
isotherm had the largest discrepancies it was selected to be
the datum and was fit to the B-W-R equation independent of
the other isotherms. When Equation 5-28 is applied to a
single isotherm it simplifies to the following expression.

$$Z = 1 + B_1 \rho_r + B_2 \rho_r^2 + B_3 \rho_r^5$$
$$+ B_4 \rho_r^2 \left(1 + B_5 \rho_r^2\right) \exp\left(-B_5 \rho_r^2\right) \tag{5-29}$$

The following values of the coefficients

$$B_1 = -1.14078 \qquad B_2 = -0.639247 \qquad B_3 = 0.086445$$
$$B_4 = 1.10566 \qquad B_5 = 0.455115$$

fit the 78 smoothed points from the $T_r = 1.05$ isotherm of the correlation with a standard error in Z of 0.0056, or 1.15 per cent. The largest discrepancy was 3.92 per cent which suggests faulty data since the B-W-R equation is capable of representing a single isotherm with much better accuracy.

With $T_r = 1.05$ taken as a datum for the isochores the temperature dependence for the product $ZT_r$ is given by the following rearrangement of the B-W-R equation

$$ZT_r = \left(ZT_r\right)_{T_r=1.05} + \left(T_r - 1.05\right)\left(1 + B_6\rho_r + B_7\rho_r^2\right)$$

$$\left(\frac{1}{T_r^2} - \frac{1}{1.05^2}\right)\left(B_8\rho_r + B_9\rho_r^2\left(1 + B_{10}\rho_r^2\right)\exp\left(-B_{10}\rho_r^2\right)\right)$$

$$(5-30)$$

To evaluate the five constants in Equation 5-30, the appropriate values for $\left(ZT_r\right)_{T_r=1.05}$ were obtained by simply multiplying both sides of Equation 5-29 by 1.05. The following values for the coefficients were obtained by minimizing the relative error in $ZT_r$.

$B_6 = 0.325610$ $\qquad$ $B_7 = 0.516982$ $\qquad$ $B_8 = -0.351376$

$B_9 = 0.322333$ $\qquad$ $B_{10} = -0.270319$

With independent variables of $\rho_r$ and $T_r$ the standard error in $ZT_r$ was 0.0215, or some 1.13 per cent. Thus, the approximation was not as accurate as Equation 5-28. However, the maximum error was reduced from 7.15 per cent for Equation 5-28 to 3.92 per cent for Equation 5-30. This slight advantage was not considered worthwhile in view of the two additional coefficients and the additional exponential term which were required in order to attain it.

The Standing and Katz correlation was also approximated

with the Martin and Hou[70] equation and various virial type
equations of state. Although the results were encouraging,
as many as 16 coefficients were required to obtain accuracy
comparable with that of the B-W-R equation. Therefore, these
equations were not pursued further.

## 5.6 Application of Some Reduced Equations of State to the Rowlinson Correlation

Rowlinson[85] presented a compressibility factor correla-
tion based on some PVT data for the inert gases (neon, argon
and xenon). The tabular correlation is a two-parameter cor-
responding states approach which uses the critical tempera-
ture and critical pressure for "reducing" the experimental
values of Z. However, unlike most corresponding states cor-
relations, Rowlinson used independent variables of reduced
temperature and pseudo-reduced density defined by

$$\rho_r = 0.293 \; RT_c/(P_c V) \tag{5-31}$$

The utility of the correlation lies in the fact that it can
be extended to other gases, with non-spherical molecules, by
a single parameter, $\delta_c$, which characterizes the effects of
orientational forces between molecules. An approximate rela-
tionship between the parameter $\delta_c$ and Pitzer's[68] acentric
factor is given by

$$\delta_c = \omega/2.4 \tag{5-32}$$

Rowlinson[86] showed that $\delta_c$ can be evaluated from a variety of
data, including: vapor pressure, second virial coefficient,
surface tension, Trouton's constant, heat capacity and recti-
linear diameter. To use the correlation for a gas, with

non-spherical molecules, the apparent-reduced temperature, $T_r'$, and apparent-reduced density, $\rho_r'$, are obtained from the relations

$$T_r' = T_r - 2\delta_c(1 - T_r) \qquad (5-33)$$

$$\rho_r' = \rho_r - \rho_r\delta_c(T_r^{-1} - 1) \qquad (5-34)$$

These modified independent variables are then used to obtain Z directly from the tabular correlation.

Since Rowlinson's correlation was presented in terms of $T_r$ and $\rho_r$, it is a convenient data source for comparing the relative accuracy of various equations of state. Some of the classical two-parameter equations of state were fitted to the correlation and the results are presented in Appendix B. The Redlich-Kwong equation was found to give the best approximation with a standard error of 1.92 per cent and a maximum error of 7.9 per cent.

The two-parameter equations did not yield the desired accuracy so equations with more coefficients were tried. The following form of the Beattie-Bridgeman[61] equation was used to approximate the correlation.

$$Z = 1 + \left(A_1 + A_2/T_r + A_3/T_r^3\right)\rho_r + \left(A_1A_4 + A_2A_5/T_r\right.$$
$$\left. + A_1A_3/T_r^3\right)\rho_r^2 + A_1A_2A_4\left(\rho_r/T_r\right)^3 \qquad (5-35)$$

The values of the coefficients obtained by minimizing the absolute error in Z were

$$A_1 = 0.5760164 \qquad A_2 = -1.6027386 \qquad A_3 = -0.07447406$$

$$A_4 = 0.1551410 \qquad A_5 = -0.2115189$$

These coefficients give a standard error in Z of 0.0086, or

1.4 per cent, with a maximum error of 11.4 per cent at the point $\rho_r$ = 1.5 on the critical isotherm. The Beattie-Bridgeman equation did not fit the critical isotherm as well as the Redlich-Kwong equation.

Next, the B-W-R equation was used to approximate the correlation. The following coefficients were obtained for Equation 5-28 by minimizing the relative error in Z.

$A_1$ = 0.3655669     $A_2$ = -0.9993822     $A_3$ = -0.5566062

$A_4$ = 0.3538158     $A_5$ = -0.4432745     $A_6$ = -0.1024061

$A_7$ = 0.5854692     $A_8$ = 0.5468492

These coefficients resulted in a standard error in Z of 0.651 per cent with a maximum error of 3.3 per cent. A pictorial comparison of this approximation with the correlation is made in Figure 5-7. The largest discrepancies occur along the high temperature isotherms ($T_r$ > 2.5). A FORTRAN subroutine called ZROWL is given in Appendix C which can be used to calculate fluid densities from Equations 5-28 and 5-31.

The B-W-R approximation of the critical region of Rowlinson's correlation was much better than it was for the Standing and Katz correlation. It may be recalled that the $T_r$ = 1.05 isotherm was taken as a datum for that correlation in a procedure to reduce the maximum errors. The same procedure was applied to Rowlinson's correlation only the critical isotherm was taken as the datum. In this case the more complex ten coefficient modification of the B-W-R equation resulted in slightly larger maximum errors. This result might have been anticipated since the B-W-R equation gave a good approximation in the vicinity of the critical. When
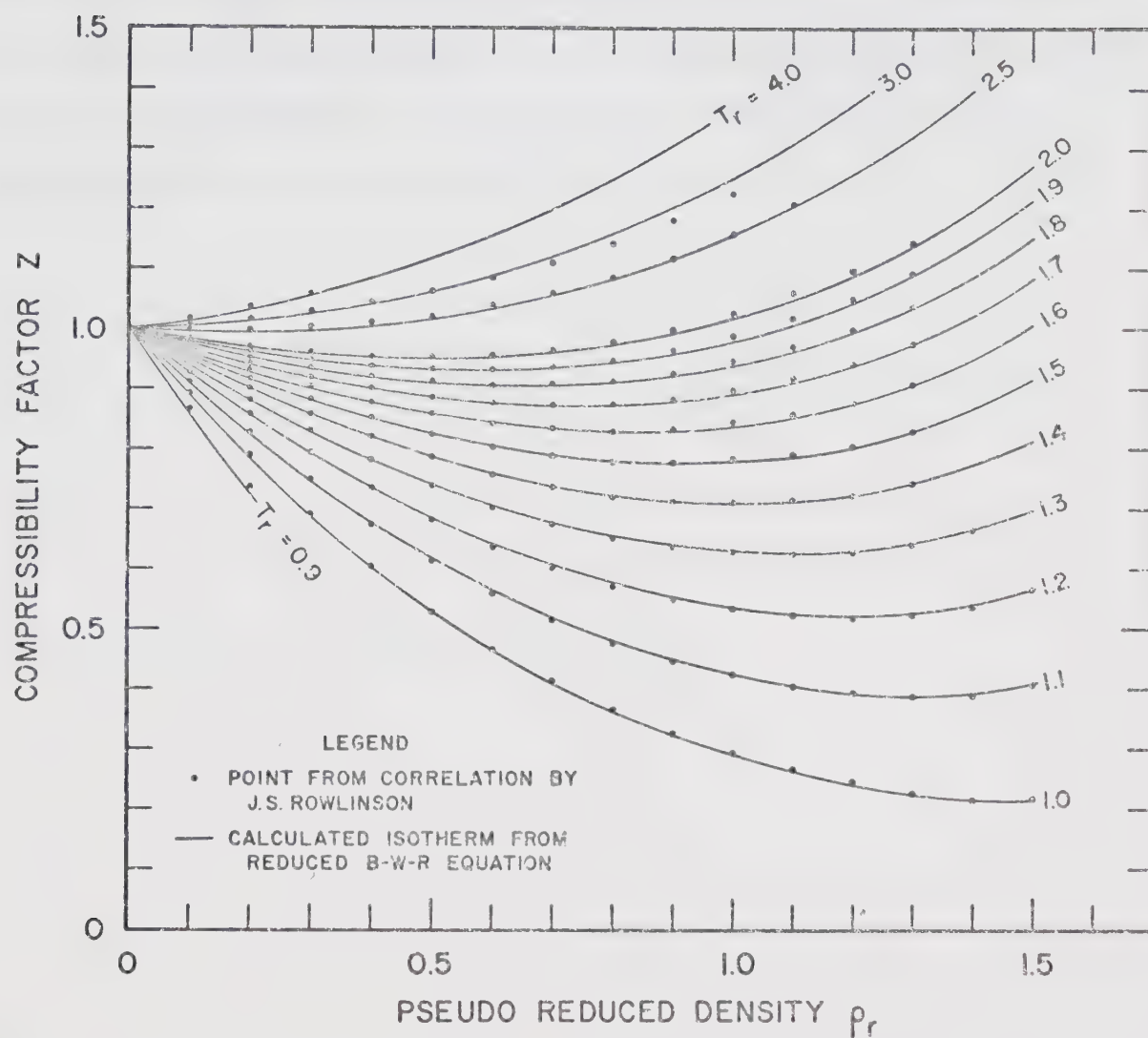
Figure 5-7.  Compressibility Factor Diagram for the
Rowlinson Correlation.

the B-W-R equation is applied in two stages, the coefficients become correlated since two separate objective functions are minimized. This problem can be avoided by evaluating the ten coefficients in Equation 5-30 simultaneously. One attempt was made at evaluating the coefficients simultaneously, however, the convergence was extremely slow and the cost of computing time did not justify further runs.

Chapter 6. SIMULATION OF EXPERIMENTAL RESULTS AND SELECTED
LITERATURE DATA

## 6.1 Foreword

This chapter discusses computer simulation results for
the depletion of a constant volume retrograde reservoir by
vapor production. A computer model was developed which direct-
ly simulates the laboratory procedure described in section 2.4
for the depletion of the unpacked cell. The computer model and
the experimental procedure both approximate the isothermal de-
pletion process by a series of equilibrium flashes. The phase
behavior portion of the computer model was described in Chap-
ter 4 and the phase density portion was discussed in Chapter
5. A FORTRAN listing of the program is given in Appendix D.

## 6.2 Simulation of Experimental Results

The composition and density of the coexisting phases of
equilibrium binary mixtures are fixed by specifying the system
temperature and pressure. Thus, the volume per cent retro-
grade liquid is the only characteristic which is free to vary
during the isothermal depletion of binary mixtures having dif-
ferent initial compositions. It may be recalled that experi-
mental and calculated retrograde liquid volumes were compared
in Tables 3-2, 3-3 and 3-4 of Chapter 3. The agreement be-
tween experimental and calculated retrograde liquid volumes
was satisfactory considering that errors at any flash are
carried forward in both the experimental procedure and the
computer simulation.

The follwoing sections discuss the computer model

approximations for K-values and phase densities of the binary
mixtures used in the experiments.

## 6.2  (a)  Methane and n-Butane Mixtures

The computer printout  for the simulation of Run 4 is
reproduced in Table 6-1.  The first part of the print out is
an echo check of some pure component data used in the calcu-
lations.  The starting composition was 0.864 mole fraction
methane and the first two flash calculations at 2000 psia
and 1750 psia indicate the system to be in the single-phase
region.  The flash at 1500 psia results in two phases with a
retrograde liquid volume of 0.91 per cent.  The calculated K-
values were 1.882 for methane and 0.249 for n-butane.  At
1500 psia the vapor and liquid phase densities were calculated
to be 0.138 ft.$^3$/lb. and 0.0407 ft.$^3$/lb., respectively.  The
results of flash calculations are presented at regular inter-
vals in Table 6-1.  The flash at 600 psia was the last to re-
main in the two-phase region.  The computer print out for the
other experimental runs with methane and n-butane are present-
ed in Tables E-1 and E-2 of Appendix E.

Extensive data for the coexisting phases of the methane
and n-butane system have been reported by Sage, Hicks and
Lacey[32].  The simulation results can be directly compared with
these data, since the phase rule requires that the composition
and density of coexisting phases be invariant with system
composition.  The phase compositions were previously compared
with published data in Figure 3-1.  A comparison of the cal-
culated K-values with those of Sage et al. is made in Figure
6-1.  The close agreement for methane results from applying

## TABLE 6-1

RUN NO. 4, METHANE AND N-BUTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------------- PURE COMPONENT DATA ------------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C4 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 0.195 | 6.770 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB[†] | LIQUID CF/LB[†] |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.864 | 0.864 | 0.000 | 1.000 | 2000.[*] | 0.00 | 0.097 | 0.0000 |
| C4 | 0.136 | 0.136 | 0.000 | 1.000 | | | | |
| MOLES | 0.471 | 0.471 | 0.000 | | 1912.[**] | | | |
| C1 | 0.865 | 0.863 | 0.000 | 1.000 | 1750. | 0.00 | 0.113 | 0.0000 |
| C4 | 0.135 | 0.135 | 0.000 | 1.000 | | | | |
| MOLES | 0.406 | 0.406 | 0.000 | | 1934. | | | |
| C1 | 0.863 | 0.869 | 0.477 | 1.822 | 1500. | 0.91 | 0.138 | 0.0407 |
| C4 | 0.135 | 0.130 | 0.522 | 0.249 | | | | |
| MOLES | 0.338 | 0.332 | 0.005 | | 1934. | | | |
| C1 | 0.862 | 0.878 | 0.396 | 2.217 | 1250. | 1.70 | 0.178 | 0.0373 |
| C4 | 0.137 | 0.121 | 0.603 | 0.201 | | | | |
| MOLES | 0.271 | 0.260 | 0.011 | | 1934. | | | |
| C1 | 0.859 | 0.877 | 0.317 | 2.767 | 1000. | 1.42 | 0.232 | 0.0348 |
| C4 | 0.140 | 0.122 | 0.682 | 0.178 | | | | |
| MOLES | 0.208 | 0.199 | 0.009 | | 1934. | | | |
| C1 | 0.853 | 0.872 | 0.253 | 3.442 | 800. | 1.01 | 0.298 | 0.0331 |
| C4 | 0.146 | 0.127 | 0.746 | 0.170 | | | | |
| MOLES | 0.161 | 0.154 | 0.006 | | 1934. | | | |
| C1 | 0.847 | 0.858 | 0.188 | 4.554 | 600. | 0.41 | 0.401 | 0.0318 |
| C4 | 0.152 | 0.141 | 0.811 | 0.174 | | | | |
| MOLES | 0.115 | 0.112 | 0.002 | | 1934. | | | |

[†] Cubic feet per pound, CF/LB

[*] System pressure, P

[**] Convergence pressure, $P_k$

TABLE 6-1    (CONT.)

RUN NO. 4, METHANE AND N-BUTANE AT 100 F.

------------------ SIMULATED DEPLETION PERFORMANCE ----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.843 | 0.843 | 0.000 | 1.000 | 400. | 0.00 | 0.608 | 0.0000 |
| C4 | 0.156 | 0.156 | 0.000 | 1.000 | | | | |
| MOLES | 0.072 | 0.072 | 0.000 | | 1934. | | | |
| C1 | 0.843 | 0.843 | 0.000 | 1.000 | 200. | 0.00 | 1.272 | 0.0000 |
| C4 | 0.156 | 0.156 | 0.000 | 1.000 | | | | |
| MOLES | 0.034 | 0.034 | 0.000 | | 1934. | | | |
| C1 | 0.843 | 0.843 | 0.000 | 1.000 | 150. | 0.00 | 1.714 | 0.0000 |
| C4 | 0.156 | 0.156 | 0.000 | 1.000 | | | | |
| MOLES | 0.025 | 0.025 | 0.000 | | 1934. | | | |
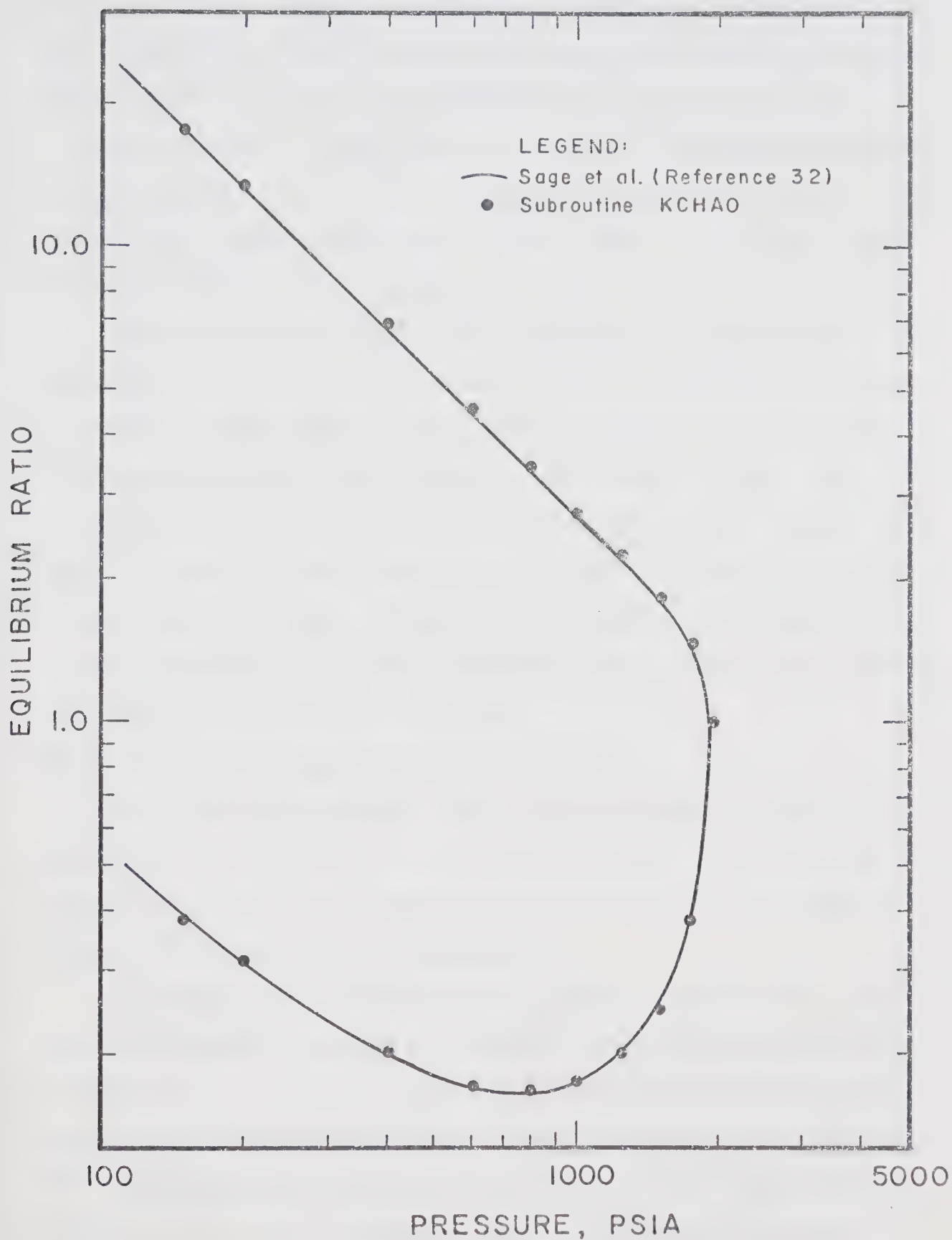
Figure 6-1.  Comparison of Calculated and Literature Equilibrium
Ratios for the Methane-n-Butane System at 100°F.

the correction ratios discussed in Section 4.4 and illustrated
in Figure 4-3. The K-values for methane and n-butane at pres-
sures above 1250 psia were obtained by extrapolating Chao-
Seader K-values at lower pressures to the convergence pressure
using Equation 4-12. The convergence pressure was calculated
to be 1934 psia by subroutine CPRES, some 22 psi higher than
the experimental value reported in reference 32.

Vapor phase densities are calculated in the computer
model by subroutine ZKATZ and are used to determine the moles
of vapor removed between equilibrium flashes. Liquid phase
densities are obtained from subroutine COMPZ and are used to
calculate the volume of retrograde liquid at each flash. Fig-
ure 6-2 makes a comparison of the calculated phase densities
with literature data. There is a systematic discrepancy in
liquid phase density which increases with pressure and amounts
to about 8 per cent at 1750 psia.

6.2 (b) Methane and n-Pentane Mixtures

The computer printout for the simulation of Run 3 is
reproduced in Table 6-2. Simulation results for the seven
other runs, with the methane-n-pentane system, are given in
Tables E-3 through E-9 of Appendix E.

A comparison of the calculated phase compositions with
the experimental results and published data was presented in
Figure 3-3. A comparison is made in Figure 6-3 between the
calculated K-values and those of Sage, Reamer, Olds and Lacey
[33]. The excellent agreement of methane K-values was attri-
buted to using the correction ratios presented in Figure
4-3. The discrepancies in the n-pentane K-values may be
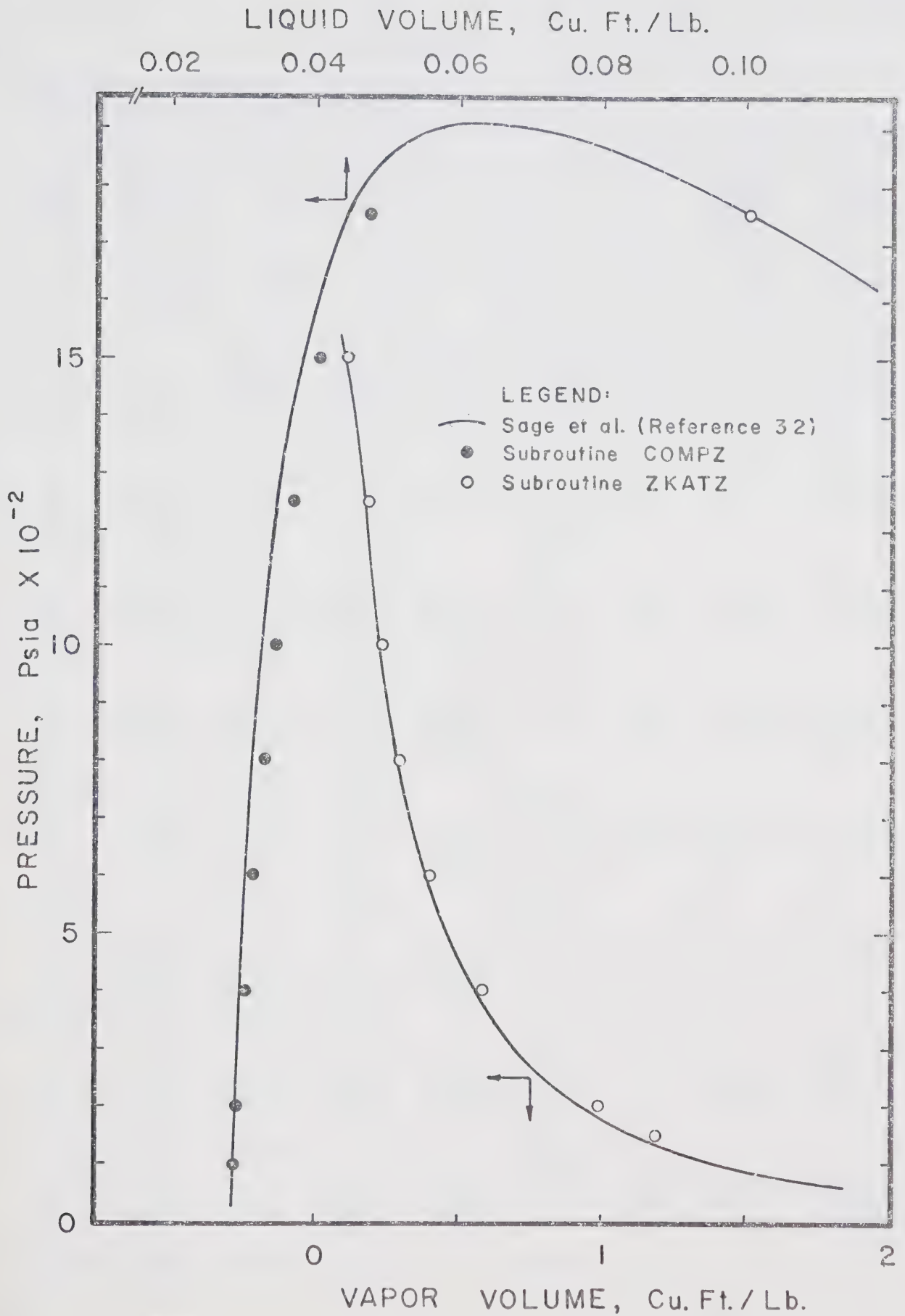
Figure 6-2.   Comparison of Calculated and Literature Phase
Densities for the Methane-n-Butane System at 100°F.

## TABLE 6-2

RUN NO. 3, METHANE AND N-PENTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------- PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|---------|------|------|--------|------|-------|-------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

--------------- SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.935 | 0.935 | 0.000 | 1.000 | 3100. | 0.00 | 0.078 | 0.0000 |
| C5 | 0.065 | 0.065 | 0.000 | 1.000 | | | | |
| MOLES | 0.649 | 0.649 | 0.000 | | 2409. | | | |
| C1 | 0.934 | 0.934 | 0.000 | 1.000 | 2500. | 0.00 | 0.093 | 0.0000 |
| C5 | 0.064 | 0.064 | 0.000 | 1.000 | | | | |
| MOLES | 0.541 | 0.541 | 0.000 | | 2409. | | | |
| C1 | 0.934 | 0.934 | 0.000 | 1.000 | 2000. | 0.00 | 0.117 | 0.0000 |
| C5 | 0.064 | 0.064 | 0.000 | 1.000 | | | | |
| MOLES | 0.432 | 0.432 | 0.000 | | 2409. | | | |
| C1 | 0.934 | 0.940 | 0.513 | 1.831 | 1750. | 0.90 | 0.139 | 0.0355 |
| C5 | 0.064 | 0.059 | 0.486 | 0.121 | | | | |
| MOLES | 0.372 | 0.366 | 0.005 | | 2409. | | | |
| C1 | 0.934 | 0.945 | 0.446 | 2.116 | 1500. | 1.36 | 0.169 | 0.0331 |
| C5 | 0.065 | 0.054 | 0.553 | 0.098 | | | | |
| MOLES | 0.312 | 0.304 | 0.008 | | 2409. | | | |
| C1 | 0.931 | 0.949 | 0.379 | 2.502 | 1250. | 1.51 | 0.212 | 0.0312 |
| C5 | 0.068 | 0.050 | 0.620 | 0.081 | | | | |
| MOLES | 0.254 | 0.245 | 0.009 | | 2409. | | | |
| C1 | 0.927 | 0.951 | 0.309 | 3.072 | 1000. | 1.50 | 0.276 | 0.0296 |
| C5 | 0.072 | 0.048 | 0.690 | 0.070 | | | | |
| MOLES | 0.198 | 0.189 | 0.009 | | 2409. | | | |

## TABLE 6-2    (CONT.)

RUN NO. 3, METHANE AND N-PENTANE AT 100 F.

-------------- SIMULATED DEPLETION PERFORMANCE --------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.921 | 0.951 | 0.251 | 3.779 | 800. | 1.39 | 0.355 | 0.0284 |
| C5 | 0.078 | 0.048 | 0.748 | 0.065 | | | | |
| MOLES | 0.156 | 0.147 | 0.008 | | 2409. | | | |
| C1 | 0.913 | 0.947 | 0.191 | 4.951 | 600. | 1.20 | 0.482 | 0.0274 |
| C5 | 0.086 | 0.052 | 0.808 | 0.064 | | | | |
| MOLES | 0.115 | 0.107 | 0.007 | | 2409. | | | |
| C1 | 0.900 | 0.937 | 0.128 | 7.288 | 400. | 0.90 | 0.721 | 0.0264 |
| C5 | 0.099 | 0.062 | 0.871 | 0.071 | | | | |
| MOLES | 0.075 | 0.070 | 0.005 | | 2409. | | | |
| C1 | 0.881 | 0.900 | 0.063 | 14.282 | 200. | 0.30 | 1.340 | 0.0256 |
| C5 | 0.118 | 0.099 | 0.936 | 0.105 | | | | |
| MOLES | 0.036 | 0.034 | 0.001 | | 2409. | | | |
| C1 | 0.860 | 0.875 | 0.046 | 18.936 | 150. | 0.11 | 1.685 | 0.0254 |
| C5 | 0.139 | 0.124 | 0.953 | 0.130 | | | | |
| MOLES | 0.026 | 0.025 | 0.000 | | 2409. | | | |
| C1 | 0.854 | 0.854 | 0.000 | 1.000 | 100. | 0.00 | 2.428 | 0.0000 |
| C5 | 0.145 | 0.145 | 0.000 | 1.000 | | | | |
| MOLES | 0.017 | 0.017 | 0.000 | | 2409. | | | |
| C1 | 0.854 | 0.854 | 0.000 | 1.000 | 80. | 0.00 | 3.049 | 0.0000 |
| C5 | 0.145 | 0.145 | 0.000 | 1.000 | | | | |
| MOLES | 0.013 | 0.013 | 0.000 | | 2409. | | | |
| C1 | 0.854 | 0.854 | 0.000 | 1.000 | 60. | 0.00 | 4.084 | 0.0000 |
| C5 | 0.145 | 0.145 | 0.000 | 1.000 | | | | |
| MOLES | 0.010 | 0.010 | 0.000 | | 2409. | | | |
| C1 | 0.854 | 0.854 | 0.000 | 1.000 | 40. | 0.00 | 6.153 | 0.0000 |
| C5 | 0.145 | 0.145 | 0.000 | 1.000 | | | | |
| MOLES | 0.006 | 0.006 | 0.000 | | 2409. | | | |
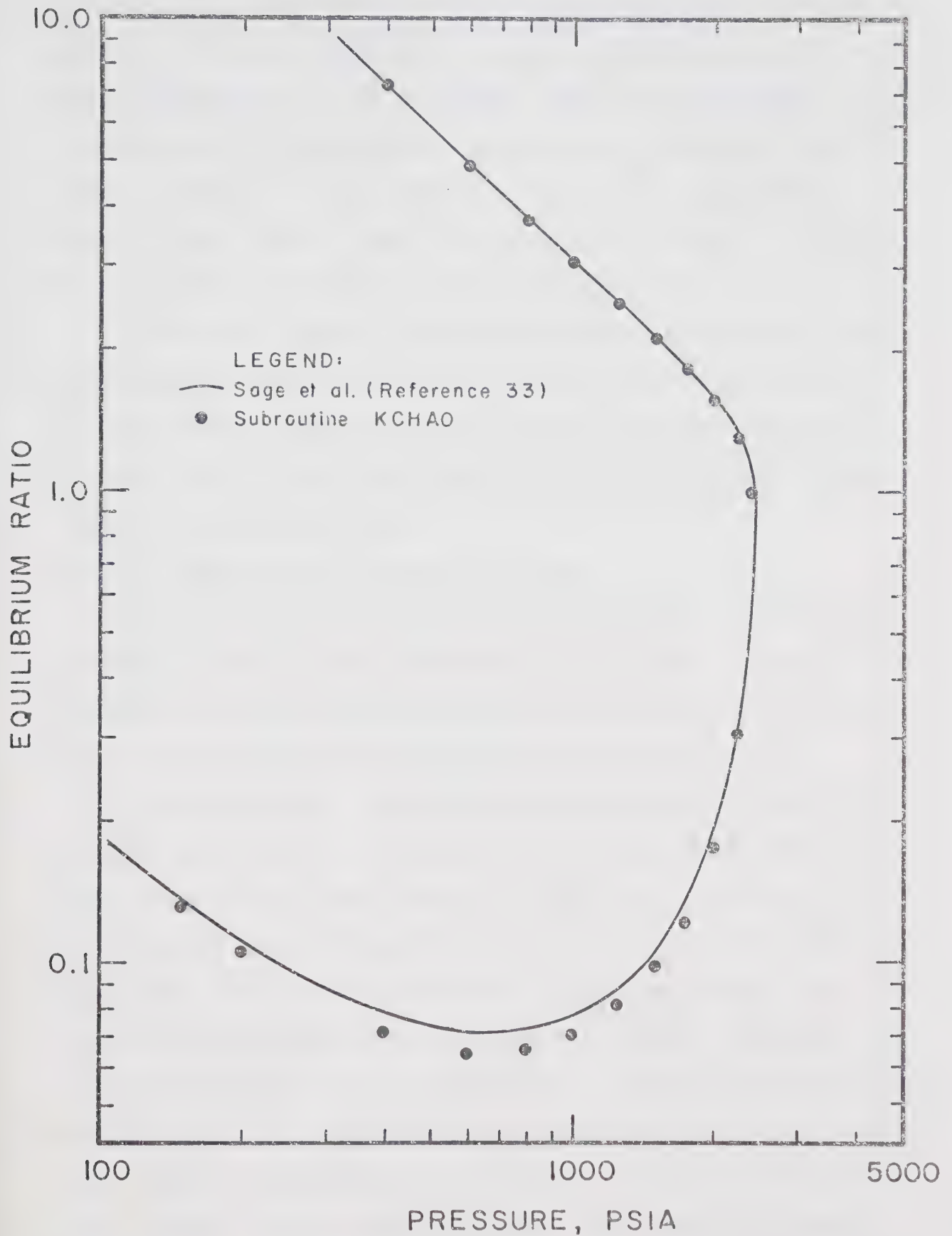
Figure 6-3. Comparison of Calculated and Literature Equilibrium Ratios for the Methane-n-Pentane System at 100°F.

caused by failure of the Redlich-Kwong equation to correctly predict the vapor phase fugacity coefficients in the Chao-Seader correlation. On the other hand, the calculated K-values result in vapor phase compositions which are about midway between those of Sage et al. and the experimental results of this work. Thus, there is some evidence to indicate that the data of Sage et al. may be in error.

Figure 6-4 makes a comparison between calculated phase densities and literature data. There is a systematic discrepancy which increases with pressure. The discrepancy at 2250 psia is 11.3 per cent for the liquid phase and 5.7 per cent for the vapor phase.

6.2 (c) Methane and n-Hexane Mixture

The print out for the computer simulation of the experimental run with methane and n-hexane is given in Table 6-3. The calculated critical pressure was 2852 psia, some 50 psi less than the value estimated by Poston and McKetta[35].

A comparison of calculated phase compositions with literature data was made in Figure 3-5 of Chapter 3. The calculated compositions and K-values differ from literature data at pressures below 200 psia, and at pressures above 2000 psia. The use of the correction ratios from Figure 4-3 forced good agreement between methane K-values, however, the calculated K-values for hexane deviate considerably from literature data. The discrepancy in convergence pressure would cause some of the difference in hexane K-values at high pressure. There is also the possibility that the vapor phase compositions of reference 25 are in error at high pressures.
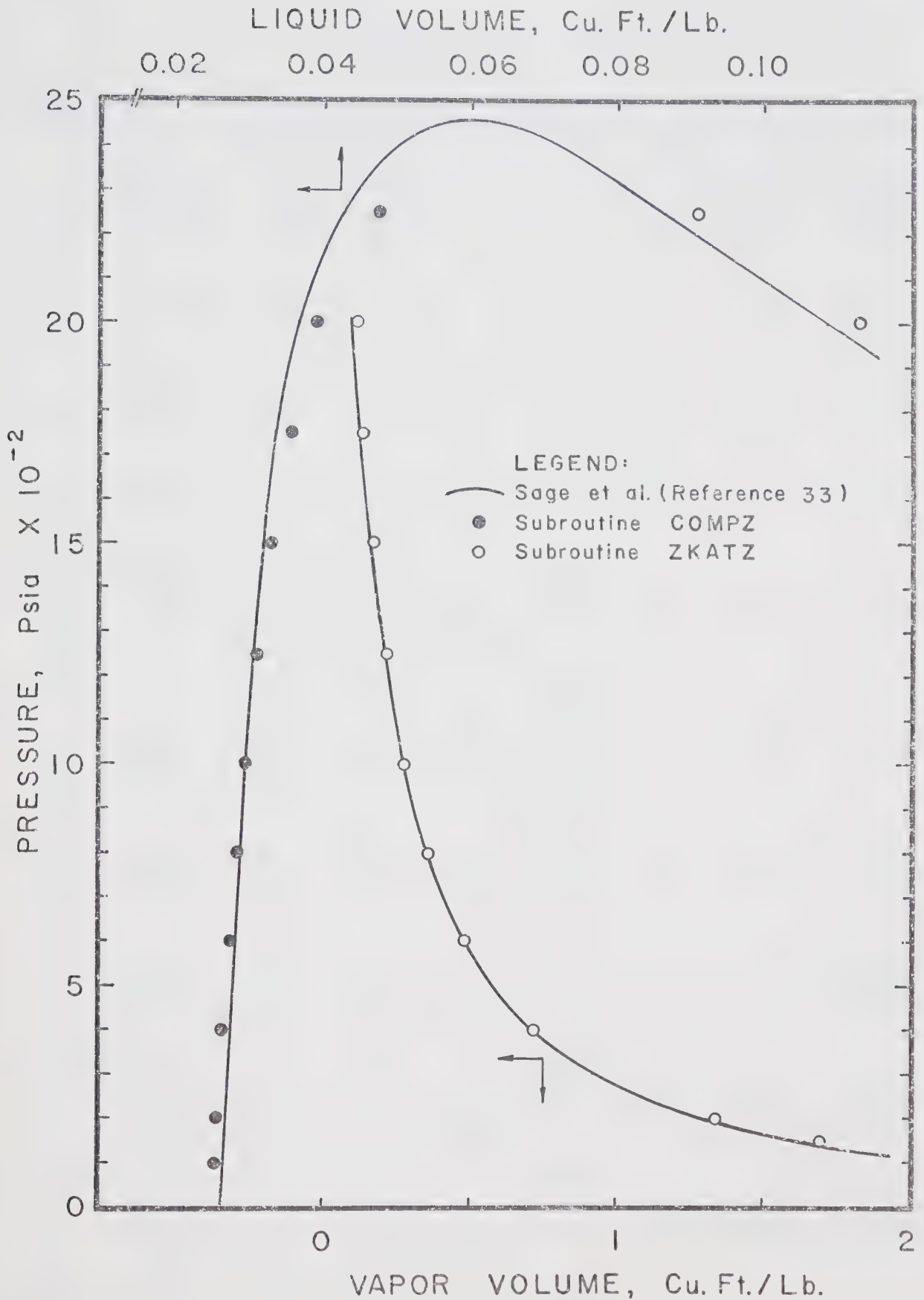
Figure 6-4.  Comparison of Calculated and Literature Phase
Densities for the Methane-n-Pentane System at 100°F.

TABLE 6-3

RUN NO. 7, METHANE AND N-HEXANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------ PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|-----------------|---------|----------|----------|-------|--------------|--------------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C6 | 86.172 | 436.6 | 5.930 | 913.14 | 0.264 | 0.292 | 7.270 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|-------------|------------|-------------|---------|---------|--------------|-------------|--------------|
| C1 | 0.930 | 0.930 | 0.000 | 1.000 | 3000. | 0.00 | 0.074 | 0.0000 |
| C6 | 0.070 | 0.070 | 0.000 | 1.000 | | | | |
| MOLES | 0.643 | 0.643 | 0.000 | | 2352. | | | |
| C1 | 0.929 | 0.940 | 0.762 | 1.232 | 2750. | 5.81 | 0.083 | 0.0479 |
| C6 | 0.069 | 0.059 | 0.237 | 0.252 | | | | |
| MOLES | 0.594 | 0.557 | 0.037 | | 2852. | | | |
| C1 | 0.929 | 0.952 | 0.633 | 1.505 | 2500. | 7.02 | 0.097 | 0.0380 |
| C6 | 0.070 | 0.047 | 0.366 | 0.128 | | | | |
| MOLES | 0.539 | 0.495 | 0.044 | | 2852. | | | |
| C1 | 0.926 | 0.964 | 0.563 | 1.711 | 2250. | 8.25 | 0.114 | 0.0349 |
| C6 | 0.073 | 0.035 | 0.436 | 0.081 | | | | |
| MOLES | 0.483 | 0.432 | 0.050 | | 2852. | | | |
| C1 | 0.922 | 0.971 | 0.508 | 1.911 | 2000. | 8.58 | 0.134 | 0.0331 |
| C6 | 0.077 | 0.028 | 0.491 | 0.052 | | | | |
| MOLES | 0.428 | 0.377 | 0.051 | | 2852. | | | |
| C1 | 0.916 | 0.973 | 0.457 | 2.128 | 1750. | 8.24 | 0.157 | 0.0318 |
| C6 | 0.083 | 0.026 | 0.542 | 0.048 | | | | |
| MOLES | 0.374 | 0.326 | 0.047 | | 2852. | | | |
| C1 | 0.907 | 0.976 | 0.404 | 2.414 | 1500. | 7.95 | 0.189 | 0.0306 |
| C6 | 0.092 | 0.023 | 0.595 | 0.039 | | | | |
| MOLES | 0.319 | 0.274 | 0.044 | | 2852. | | | |

## TABLE 6-3    (CONT.)

RUN NO. 7, METHANE AND N-HEXANE AT 100 F.

----------------- SIMULATED DEPLETION PERFORMANCE -----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.895 | 0.978 | 0.347 | 2.812 | 1250. | 7.62 | 0.235 | 0.0294 |
| C6 | 0.104 | 0.021 | 0.652 | 0.032 | | | | |
| MOLES | 0.265 | 0.223 | 0.041 | | 2852. | | | |
| C1 | 0.879 | 0.980 | 0.287 | 3.407 | 1000. | 7.27 | 0.304 | 0.0283 |
| C6 | 0.120 | 0.019 | 0.712 | 0.027 | | | | |
| MOLES | 0.213 | 0.174 | 0.038 | | 2852. | | | |
| C1 | 0.854 | 0.980 | 0.236 | 4.150 | 800. | 6.96 | 0.390 | 0.0273 |
| C6 | 0.145 | 0.019 | 0.763 | 0.024 | | | | |
| MOLES | 0.173 | 0.136 | 0.036 | | 2852. | | | |
| C1 | 0.825 | 0.980 | 0.181 | 5.397 | 600. | 6.64 | 0.532 | 0.0268 |
| C6 | 0.174 | 0.019 | 0.818 | 0.023 | | | | |
| MOLES | 0.134 | 0.100 | 0.032 | | 2852. | | | |
| C1 | 0.780 | 0.977 | 0.124 | 7.862 | 400. | 6.29 | 0.809 | 0.0261 |
| C6 | 0.219 | 0.022 | 0.875 | 0.025 | | | | |
| MOLES | 0.096 | 0.065 | 0.031 | | 2852. | | | |
| C1 | 0.703 | 0.966 | 0.063 | 15.290 | 200. | 5.85 | 1.585 | 0.0254 |
| C6 | 0.296 | 0.033 | 0.936 | 0.036 | | | | |
| MOLES | 0.060 | 0.032 | 0.028 | | 2852. | | | |
| C1 | 0.545 | 0.940 | 0.031 | 30.142 | 100. | 5.53 | 2.929 | 0.0250 |
| C6 | 0.454 | 0.059 | 0.968 | 0.060 | | | | |
| MOLES | 0.042 | 0.015 | 0.026 | | 2852. | | | |
| C1 | 0.375 | 0.890 | 0.014 | 59.824 | 50. | 5.27 | 5.006 | 0.0249 |
| C6 | 0.624 | 0.109 | 0.985 | 0.111 | | | | |
| MOLES | 0.032 | 0.007 | 0.024 | | 2852. | | | |
| C1 | 0.227 | 0.787 | 0.006 | 119.098 | 25. | 5.02 | 7.710 | 0.0248 |
| C6 | 0.772 | 0.212 | 0.993 | 0.213 | | | | |
| MOLES | 0.027 | 0.003 | 0.023 | | 2852. | | | |

It may be recalled that the data of Poston and McKetta indicated an unusually sharp reversal of the dew point locus to the critical state. Coexisting phase density data for the methane-n-hexane system could not be found in the literature so a comparison with calculated phase densities was not possible.

## 6.3 Simulated Depletion Performance of Some Ternary Mixtures

The computer model was used to simulate the depletion performance of four ternary systems. Although the program could be used for any ternary mixture of alkanes from methane through decane, only systems for which there were PVT data in the literature were studied. Compositions of the initial mixtures were selected to result in typical retrograde behavior. For this work the Chao-Seader K-values for methane were used directly without applying correction ratios of the type discussed in Section 4.4.

The phase rule requires that three intensive properties be specified to define the two-phase region of a ternary mixture. Since three properties must be specified, some interpolation is usually required to make a comparison with literature data for ternary systems. This is particularly true for the simulation of the depletion performance of a retrograde system where the overall composition is continuously changing.

Literature data for ternary systems is often correlated in terms of a composition parameter, C, defined as

$$C = x_i/(x_i + x_h) \tag{6-1}$$

where: $x_i$ is the mole fraction of intermediate component in the liquid phase,

$x_h$ is the mole fraction of heavy component in the liquid phase.

This definition is useful when K-values are correlated with convergence pressures calculated by Hadden's method[44], but is of limited use when the critical composition method is used to calculate convergence pressures. The following sections compare the calculated results for the example depletions with literature data whenever possible.

6.2 (a) Methane, Propane and n-Butane Mixtures

Data on the phase equilibria in the methane, propane and n-butane system at temperatures of 40°, 100°, 160° and 220°F have been reported by Wiese, Jacobs and Sage[87]. Example depletion performance calculations were made for this system at temperatures of 40°, 100° and 160°F. The computer print-out for the example at 40°F is presented in Table 6-4. The printout for the examples at 100°F and 160°F may be found in Tables E-10 and E-11 of Appendix E.

Table 6-4 indicates a retrograde dew point of approximately 1600 psia and a calculated convergence pressure of 1801 psia. The calculated phase compositions do not agree very well with those of reference 87 for the pressures greater than 1000 psia. The calculated convergence pressure is the cause of the discrepancies. The data of reference 87 indicate the critical pressure of the critical composition for the mixture to be approximately 1600 psia. Thus, the calculated K-values for pressures greater than 1000 psia were obtained by extrapolation to a convergence pressure which was too high. Figure 6-5 illustrates the systematic deviation of

## TABLE 6-4

METHANE, PROPANE, AND N-BUTANE MIXTURE AT 40 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------ PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|---------|---------|----------|----------|-------|--------|--------|
| C1   | 16.042  | 669.7   | 1.590    | 343.13   | 0.288 | 0.000  | 5.860  |
| C3   | 44.094  | 616.3   | 3.210    | 665.68   | 0.276 | 0.153  | 6.540  |
| C4   | 58.120  | 550.7   | 4.080    | 765.29   | 0.274 | 0.195  | 6.770  |

----------------- SIMULATED DEPLETION PERFORMANCE -----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|-------|-------|-------|-------|-------|------|-------|--------|
| C1   | 0.825 | 0.825 | 0.000 | 1.000 | 1650. | 0.00 | 0.081 | 0.0000 |
| C3   | 0.105 | 0.105 | 0.000 | 1.000 |       |      |       |        |
| C4   | 0.070 | 0.070 | 0.000 | 1.000 |       |      |       |        |
| MOLES | 0.556 | 0.556 | 0.000 |      | 1801. |      |       |        |
| C1   | 0.824 | 0.825 | 0.515 | 1.601 | 1600. | 0.05 | 0.085 | 0.0395 |
| C3   | 0.104 | 0.104 | 0.235 | 0.445 |       |      |       |        |
| C4   | 0.069 | 0.069 | 0.249 | 0.280 |       |      |       |        |
| MOLES | 0.536 | 0.536 | 0.000 |      | 1801. |      |       |        |
| C1   | 0.824 | 0.842 | 0.479 | 1.756 | 1500. | 3.34 | 0.099 | 0.0391 |
| C3   | 0.105 | 0.097 | 0.250 | 0.390 |       |      |       |        |
| C4   | 0.070 | 0.060 | 0.270 | 0.222 |       |      |       |        |
| MOLES | 0.482 | 0.456 | 0.025 |      | 1801. |      |       |        |
| C1   | 0.823 | 0.872 | 0.418 | 2.086 | 1250. | 6.95 | 0.144 | 0.0362 |
| C3   | 0.105 | 0.084 | 0.278 | 0.303 |       |      |       |        |
| C4   | 0.071 | 0.042 | 0.302 | 0.141 |       |      |       |        |
| MOLES | 0.371 | 0.319 | 0.052 |      | 1801. |      |       |        |
| C1   | 0.808 | 0.888 | 0.361 | 2.458 | 1000. | 7.57 | 0.206 | 0.0348 |
| C3   | 0.112 | 0.077 | 0.305 | 0.253 |       |      |       |        |
| C4   | 0.079 | 0.034 | 0.333 | 0.102 |       |      |       |        |
| MOLES | 0.284 | 0.228 | 0.056 |      | 1801. |      |       |        |
| C1   | 0.783 | 0.890 | 0.334 | 2.660 | 900.  | 7.35 | 0.237 | 0.0341 |
| C3   | 0.122 | 0.077 | 0.315 | 0.243 |       |      |       |        |
| C4   | 0.093 | 0.032 | 0.349 | 0.094 |       |      |       |        |
| MOLES | 0.253 | 0.199 | 0.054 |      | 1801. |      |       |        |

## TABLE 6-4    (CONT.)

METHANE, PROPANE, AND N-BUTANE MIXTURE AT 40 F.

```
-------------- SIMULATED DEPLETION PERFORMANCE --------------
       SYSTEM  VAPOR   LIQUID    K     P, PK  LIQ    VAPOR   LIQUID
COMP    COMP    COMP    COMP   VALUE   PSIA  VOL %   CF/LB   CF/LB
----    ----    ----    ----   -----   ----- ----    -----   -----
```

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|-------------|------------|-------------|---------|------------|-----------|-------------|--------------|
| C1 | 0.770 | 0.890 | 0.305 | 2.914 | 800. | 7.03 | 0.275 | 0.0334 |
| C3 | 0.128 | 0.077 | 0.326 | 0.238 | | | | |
| C4 | 0.100 | 0.032 | 0.368 | 0.087 | | | | |
| MOLES | 0.223 | 0.172 | 0.051 | | 1801. | | | |
| C1 | 0.755 | 0.887 | 0.273 | 3.242 | 700. | 6.62 | 0.323 | 0.0327 |
| C3 | 0.134 | 0.079 | 0.335 | 0.237 | | | | |
| C4 | 0.109 | 0.032 | 0.390 | 0.083 | | | | |
| MOLES | 0.195 | 0.147 | 0.048 | | 1800. | | | |
| C1 | 0.735 | 0.882 | 0.239 | 3.681 | 600. | 6.17 | 0.384 | 0.0320 |
| C3 | 0.143 | 0.083 | 0.344 | 0.242 | | | | |
| C4 | 0.121 | 0.033 | 0.416 | 0.081 | | | | |
| MOLES | 0.167 | 0.123 | 0.044 | | 1799. | | | |
| C1 | 0.711 | 0.873 | 0.203 | 4.300 | 500. | 5.66 | 0.466 | 0.0312 |
| C3 | 0.152 | 0.089 | 0.350 | 0.255 | | | | |
| C4 | 0.135 | 0.036 | 0.445 | 0.082 | | | | |
| MOLES | 0.141 | 0.100 | 0.040 | | 1797. | | | |
| C1 | 0.681 | 0.858 | 0.164 | 5.232 | 400. | 5.09 | 0.582 | 0.0305 |
| C3 | 0.164 | 0.099 | 0.354 | 0.280 | | | | |
| C4 | 0.154 | 0.041 | 0.481 | 0.086 | | | | |
| MOLES | 0.115 | 0.079 | 0.036 | | 1792. | | | |
| C1 | 0.641 | 0.832 | 0.122 | 6.792 | 300. | 4.44 | 0.762 | 0.0297 |
| C3 | 0.179 | 0.115 | 0.351 | 0.330 | | | | |
| C4 | 0.179 | 0.051 | 0.526 | 0.097 | | | | |
| MOLES | 0.089 | 0.058 | 0.031 | | 1783. | | | |
| C1 | 0.586 | 0.782 | 0.078 | 9.924 | 200. | 3.62 | 1.081 | 0.0289 |
| C3 | 0.197 | 0.145 | 0.332 | 0.436 | | | | |
| C4 | 0.216 | 0.072 | 0.588 | 0.123 | | | | |
| MOLES | 0.063 | 0.038 | 0.024 | | 1759. | | | |
| C1 | 0.505 | 0.650 | 0.033 | 19.347 | 100. | 2.21 | 1.832 | 0.0280 |
| C3 | 0.219 | 0.204 | 0.265 | 0.769 | | | | |
| C4 | 0.275 | 0.145 | 0.700 | 0.207 | | | | |
| MOLES | 0.034 | 0.019 | 0.014 | | 1682. | | | |
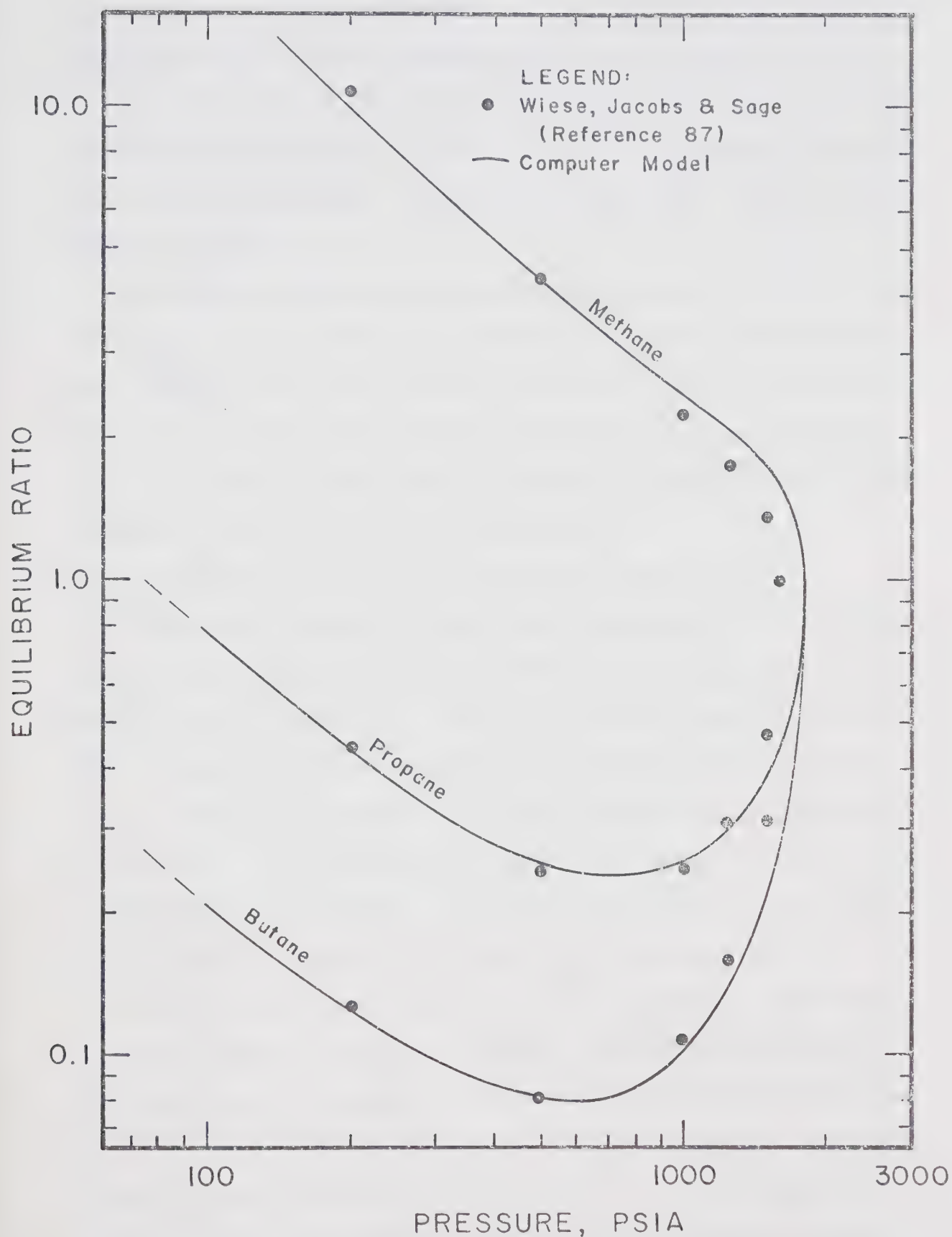
Figure 6-5. Comparison of Calculated and Literature Equilib-
rium Ratios for the Methane-Propane-n-Butane
Mixtures of Table 6-4.

the K-values at high pressures. The circles on the figure represent the K-values interpolated from the data of Wiese et al. using composition parameters determined from the liquid phase compositions of Table 6-4. It is apparent that if the correct convergence pressure was used, the K-values would compare favorably.

The calculated convergence pressures were 1724 psia and 1443 psia for the examples at 100°F and 160°F, respectively. These values were also too high compared to the data of Wiese et al. which indicated critical pressures of approximately 1550 psia and 1300 psia for the critical compositions of the examples at 100°F and 160°F, respectively.

6.3   (b) Methane, Propane and n-Pentane Mixtures

Phase equilibria data have been reported for the methane, propane and n-pentane system at 100°F by Carter, Sage and Lacey[88], and at 160°F and 220°F by Dourson, Sage and Lacey[89]. Three example depletion performance calculations were made, one for each of the temperatures for which there were experimental data. The computer printout for the example at 100°F is presented in Table 6-5. The examples for 160°F and 220°F may be found in Tables E-12 and E-13 of Appendix E.

The starting composition for the example at 100°F was 0.8 mole fraction methane, 0.12 mole fraction propane and 0.08 mole fraction n-pentane. The calculated retrograde dew point was approximately 1800 psia. The convergence pressure of the critical mixture was calculated to be 2088 psia compared to a value of 2200 psia interpolated from the experimental data of reference 88. Since the discrepancy in

## TABLE 6-5

METHANE, PROPANE, AND N-PENTANE MIXTURE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------ PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C3 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 0.153 | 6.540 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.800 | 0.800 | 0.000 | 1.000 | 2000. | 0.00 | 0.081 | 0.0000 |
| C3 | 0.120 | 0.120 | 0.000 | 1.000 | | | | |
| C5 | 0.080 | 0.080 | 0.000 | 1.000 | | | | |
| MOLES 0.513 | 0.513 | 0.000 | | | 2088. | | | |
| C1 | 0.799 | 0.818 | 0.447 | 1.828 | 1750. | 3.82 | 0.101 | 0.0368 |
| C3 | 0.119 | 0.114 | 0.226 | 0.506 | | | | |
| C5 | 0.079 | 0.067 | 0.326 | 0.205 | | | | |
| MOLES 0.438 | 0.412 | 0.025 | | | 2088. | | | |
| C1 | 0.796 | 0.843 | 0.391 | 2.152 | 1500. | 6.85 | 0.134 | 0.0349 |
| C3 | 0.120 | 0.106 | 0.242 | 0.441 | | | | |
| C5 | 0.082 | 0.049 | 0.365 | 0.135 | | | | |
| MOLES 0.362 | 0.317 | 0.045 | | | 2088. | | | |
| C1 | 0.787 | 0.855 | 0.344 | 2.486 | 1250. | 7.46 | 0.176 | 0.0337 |
| C3 | 0.123 | 0.103 | 0.256 | 0.403 | | | | |
| C5 | 0.089 | 0.041 | 0.399 | 0.102 | | | | |
| MOLES 0.295 | 0.247 | 0.048 | | | 2088. | | | |
| C1 | 0.771 | 0.859 | 0.289 | 2.972 | 1000. | 7.10 | 0.234 | 0.0322 |
| C3 | 0.128 | 0.103 | 0.265 | 0.389 | | | | |
| C5 | 0.099 | 0.037 | 0.444 | 0.083 | | | | |
| MOLES 0.233 | 0.188 | 0.045 | | | 2090. | | | |
| C1 | 0.748 | 0.856 | 0.239 | 3.580 | 800. | 6.48 | 0.303 | 0.0309 |
| C3 | 0.135 | 0.106 | 0.268 | 0.398 | | | | |
| C5 | 0.116 | 0.036 | 0.492 | 0.074 | | | | |
| MOLES 0.186 | 0.145 | 0.040 | | | 2090. | | | |

## TABLE 6-5    (CONT.)

METHANE, PROPANE, AND N-PENTANE MIXTURE AT 100 F.

---------------- SIMULATED DEPLETION PERFORMANCE ----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.721 | 0.846 | 0.184 | 4.597 | 600. | 5.67 | 0.413 | 0.0295 |
| C3 | 0.142 | 0.114 | 0.261 | 0.437 | | | | |
| C5 | 0.136 | 0.039 | 0.554 | 0.071 | | | | |
| MOLES | 0.141 | 0.106 | 0.035 | | 2088. | | | |
| C1 | 0.681 | 0.836 | 0.154 | 5.414 | 500. | 5.24 | 0.495 | 0.0289 |
| C3 | 0.151 | 0.120 | 0.253 | 0.477 | | | | |
| C5 | 0.167 | 0.042 | 0.592 | 0.072 | | | | |
| MOLES | 0.119 | 0.087 | 0.032 | | 2084. | | | |
| C1 | 0.652 | 0.821 | 0.123 | 6.644 | 400. | 4.75 | 0.613 | 0.0282 |
| C3 | 0.156 | 0.130 | 0.239 | 0.542 | | | | |
| C5 | 0.190 | 0.048 | 0.636 | 0.076 | | | | |
| MOLES | 0.098 | 0.069 | 0.028 | | 2075. | | | |
| C1 | 0.615 | 0.796 | 0.091 | 8.700 | 300. | 4.21 | 0.797 | 0.0274 |
| C3 | 0.162 | 0.143 | 0.217 | 0.658 | | | | |
| C5 | 0.221 | 0.059 | 0.690 | 0.086 | | | | |
| MOLES | 0.076 | 0.051 | 0.025 | | 2058. | | | |
| C1 | 0.564 | 0.753 | 0.058 | 12.826 | 200. | 3.54 | 1.125 | 0.0267 |
| C3 | 0.167 | 0.162 | 0.181 | 0.899 | | | | |
| C5 | 0.267 | 0.083 | 0.760 | 0.109 | | | | |
| MOLES | 0.054 | 0.033 | 0.020 | | 2025. | | | |
| C1 | 0.489 | 0.714 | 0.042 | 16.956 | 150. | 3.14 | 1.413 | 0.0262 |
| C3 | 0.169 | 0.177 | 0.154 | 1.144 | | | | |
| C5 | 0.340 | 0.107 | 0.802 | 0.134 | | | | |
| MOLES | 0.043 | 0.025 | 0.018 | | 1991. | | | |
| C1 | 0.432 | 0.647 | 0.025 | 25.225 | 100. | 2.62 | 1.905 | 0.0258 |
| C3 | 0.167 | 0.193 | 0.118 | 1.635 | | | | |
| C5 | 0.399 | 0.158 | 0.855 | 0.184 | | | | |
| MOLES | 0.031 | 0.016 | 0.015 | | 1933. | | | |

ZKATZ ITER = 0

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.353 | 0.490 | 0.009 | 50.016 | 50. | 1.60 | 2.957 | 0.0253 |
| C3 | 0.158 | 0.196 | 0.063 | 3.111 | | | | |
| C5 | 0.488 | 0.313 | 0.927 | 0.337 | | | | |
| MOLES | 0.017 | 0.008 | 0.009 | | 1820. | | | |

convergence pressure was about 5 per cent for this case, we might expect better agreement between the calculated and experimental K-values at high pressure. Figure 6-6 tends to confirm this expectation since there is satisfactory agreement for propane and n-pentane. Discrepancies in the methane K-values are likely caused by the type of systematic deviation that was discussed in Section 4.4.

There was satisfactory agreement between the data of reference 88 and the calculated data (convergence pressure and K-values) for the example at 160°F. However, the agreement between calculations and experimental data was not as good at 220°F. Propane was supercritical at 220°F so the Chao-Seader K-values were not as accurate as those at temperatures of 100°F and 160°F. A valid comparison of convergence pressure could not be made at 220°F since the experimental data are rather sparce at this temperature.

## 6.3 (c) Methane, Propane and Decane Mixtures

Phase equilibria data for the methane, propane and decane system at temperatures of 40°, 100°, 280°, 400° and 460°F were reported by Wiese, Reamer and Sage[90]. Two example depletion performance calculations were performed; Table 6-6 gives the computer printout for an example at 100°F, and Table E-14 of Appendix E gives the printout for an example at 280°F.

Table 6-6 indicates a retrograde dew point of some 3400 psia. The calculated convergence pressure of 3957 psia compares favorably with a value of approximately 4100 psia from the experimental data of Wiese et al. Figure 6-7 makes a
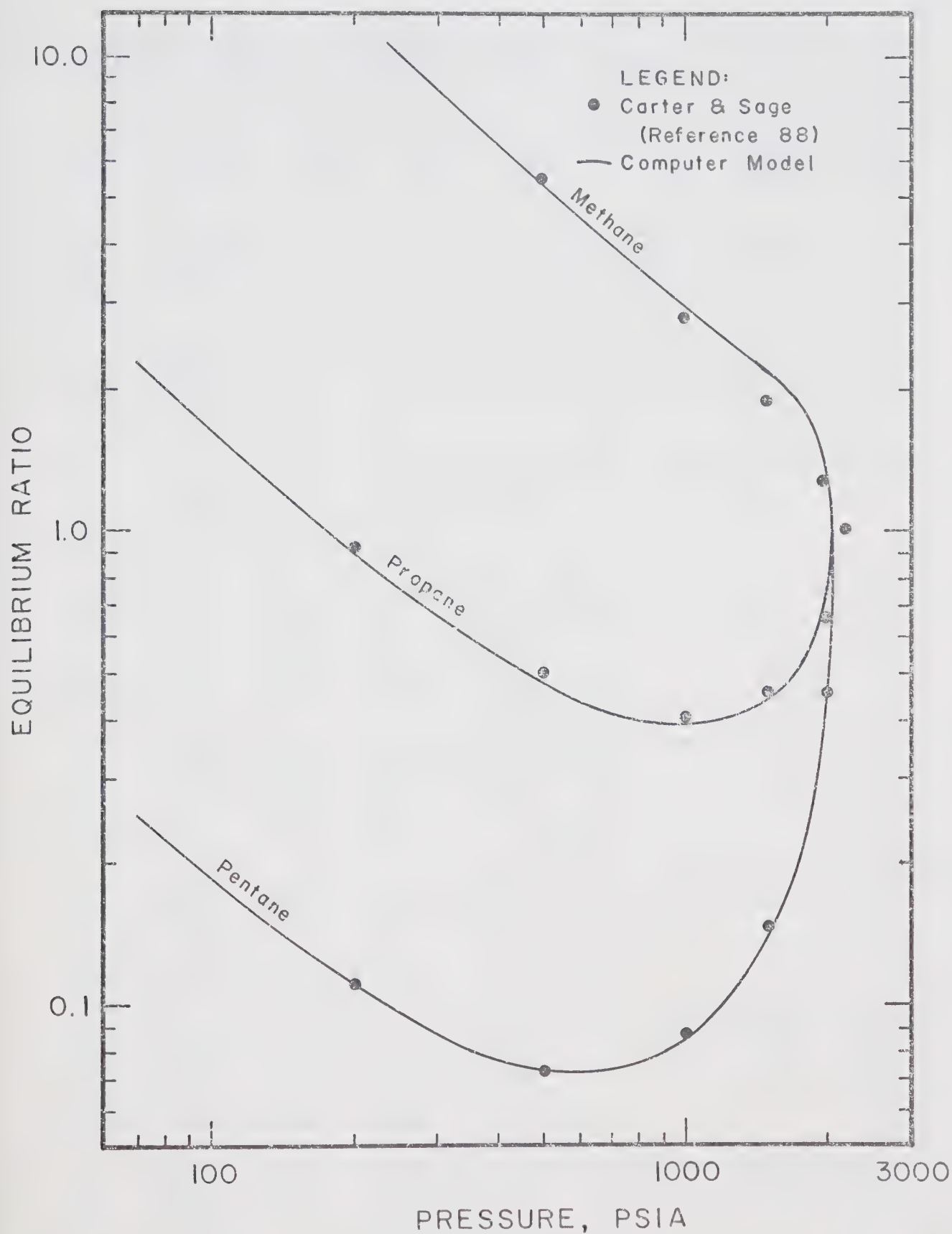
Figure 6-6.   Comparison of Calculated and Literature Equilib-
              rium Ratios for the Methane-Propane-n-Pentane
              Mixtures of Table 6-5.

# TABLE 6-6.

METHANE, PROPANE, N-DECANE MIXTURE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

---------------------------- PURE COMPONENT DATA ----------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1   | 16.042  | 669.7 | 1.590 | 343.13  | 0.288 | 0.000 | 5.860 |
| C3   | 44.094  | 616.3 | 3.210 | 665.68  | 0.276 | 0.153 | 6.540 |
| C10  | 142.276 | 304.0 | 9.660 | 1111.70 | 0.246 | 0.486 | 8.180 |

-------------- SIMULATED DEPLETION PERFORMANCE --------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1   | 0.900 | 0.900 | 0.000 | 1.0000 | 3750. | 0.00 | 0.057 | 0.0000 |
| C3   | 0.060 | 0.060 | 0.000 | 1.0000 |       |      |       |        |
| C10  | 0.040 | 0.040 | 0.000 | 1.0000 |       |      |       |        |
| MOLES | 0.759 | 0.759 | 0.000 |       | 3957. |      |       |        |
| C1   | 0.899 | 0.899 | 0.000 | 1.0000 | 3500. | 0.00 | 0.060 | 0.0000 |
| C3   | 0.059 | 0.059 | 0.000 | 1.0000 |       |      |       |        |
| C10  | 0.039 | 0.039 | 0.000 | 1.0000 |       |      |       |        |
| MOLES | 0.729 | 0.729 | 0.000 |       | 3957. |      |       |        |
| C1   | 0.899 | 0.910 | 0.609 | 1.4931 | 3250. | 4.40 | 0.067 | 0.0324 |
| C3   | 0.059 | 0.058 | 0.103 | 0.5638 |       |      |       |        |
| C10  | 0.039 | 0.031 | 0.286 | 0.1094 |       |      |       |        |
| MOLES | 0.681 | 0.657 | 0.024 |       | 3957. |      |       |        |
| C1   | 0.899 | 0.921 | 0.575 | 1.6010 | 3000. | 8.23 | 0.077 | 0.0313 |
| C3   | 0.060 | 0.056 | 0.108 | 0.5218 |       |      |       |        |
| C10  | 0.040 | 0.021 | 0.315 | 0.0678 |       |      |       |        |
| MOLES | 0.629 | 0.584 | 0.044 |       | 3957. |      |       |        |
| C1   | 0.897 | 0.937 | 0.513 | 1.8249 | 2500. | 11.73 | 0.101 | 0.0298 |
| C3   | 0.060 | 0.054 | 0.118 | 0.4558 |       |       |       |        |
| C10  | 0.042 | 0.008 | 0.367 | 0.0219 |       |       |       |        |
| MOLES | 0.526 | 0.466 | 0.059 |       | 3957. |       |       |        |
| C1   | 0.889 | 0.945 | 0.446 | 2.1162 | 2000. | 12.33 | 0.136 | 0.0284 |
| C3   | 0.061 | 0.052 | 0.130 | 0.4068 |       |       |       |        |
| C10  | 0.048 | 0.001 | 0.423 | 0.0031 |       |       |       |        |
| MOLES | 0.422 | 0.363 | 0.059 |       | 3957. |       |       |        |

## TABLE 6-6. (CONT.)

METHANE, PROPANE, N-DECANE MIXTURE AT 100 F.

------------- SIMULATED DEPLETION PERFORMANCE -------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK VOL % | LIQ VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1  | 0.875 | 0.945 | 0.366 | 2.5842 | 1500. | 11.36 | 0.188 | 0.0269 |
| C3  | 0.063 | 0.053 | 0.140 | 0.3765 |       |       |       |        |
| C10 | 0.060 | 0.000 | 0.492 | 0.0018 |       |       |       |        |
| MOLES | 0.318 | 0.266 | 0.051 |      | 3957. |       |       |        |
|     |       |       |       |        |       |       |       |        |
| C1  | 0.852 | 0.944 | 0.266 | 3.5465 | 1000. | 10.33 | 0.297 | 0.0254 |
| C3  | 0.067 | 0.055 | 0.145 | 0.3790 |       |       |       |        |
| C10 | 0.080 | 0.000 | 0.588 | 0.0010 |       |       |       |        |
| MOLES | 0.213 | 0.170 | 0.043 |      | 3951. |       |       |        |
|     |       |       |       |        |       |       |       |        |
| C1  | 0.807 | 0.942 | 0.220 | 4.2791 | 800. | 9.89 | 0.379 | 0.0247 |
| C3  | 0.073 | 0.057 | 0.142 | 0.4021 |       |       |       |        |
| C10 | 0.118 | 0.000 | 0.637 | 0.0008 |       |       |       |        |
| MOLES | 0.173 | 0.133 | 0.039 |      | 3940. |       |       |        |
|     |       |       |       |        |       |       |       |        |
| C1  | 0.776 | 0.938 | 0.170 | 5.5099 | 600. | 9.43 | 0.516 | 0.0240 |
| C3  | 0.076 | 0.061 | 0.134 | 0.4548 |       |       |       |        |
| C10 | 0.146 | 0.000 | 0.694 | 0.0007 |       |       |       |        |
| MOLES | 0.134 | 0.098 | 0.036 |      | 3916. |       |       |        |
|     |       |       |       |        |       |       |       |        |
| C1  | 0.730 | 0.930 | 0.116 | 7.9885 | 400. | 8.97 | 0.786 | 0.0233 |
| C3  | 0.081 | 0.068 | 0.119 | 0.5787 |       |       |       |        |
| C10 | 0.188 | 0.000 | 0.764 | 0.0006 |       |       |       |        |
| MOLES | 0.097 | 0.064 | 0.033 |      | 3866. |       |       |        |
|     |       |       |       |        |       |       |       |        |
| C1  | 0.653 | 0.913 | 0.059 | 15.4718 | 200. | 8.46 | 1.573 | 0.0226 |
| C3  | 0.086 | 0.085 | 0.087 | 0.9826 |       |       |       |        |
| C10 | 0.260 | 0.000 | 0.353 | 0.0007 |       |       |       |        |
| MOLES | 0.061 | 0.031 | 0.029 |      | 3744. |       |       |        |
|     |       |       |       |        |       |       |       |        |
| C1  | 0.498 | 0.890 | 0.029 | 30.4896 | 100. | 8.18 | 3.076 | 0.0221 |
| C3  | 0.086 | 0.108 | 0.059 | 1.8117 |       |       |       |        |
| C10 | 0.415 | 0.001 | 0.910 | 0.0011 |       |       |       |        |
| MOLES | 0.043 | 0.015 | 0.027 |      | 3561. |       |       |        |
|     |       |       |       |        |       |       |       |        |
| C1  | 0.338 | 0.860 | 0.014 | 60.5808 | 50. | 8.01 | 5.909 | 0.0219 |
| C3  | 0.077 | 0.137 | 0.039 | 3.4799 |       |       |       |        |
| C10 | 0.584 | 0.001 | 0.946 | 0.0020 |       |       |       |        |
| MOLES | 0.034 | 0.007 | 0.026 |      | 3321. |       |       |        |
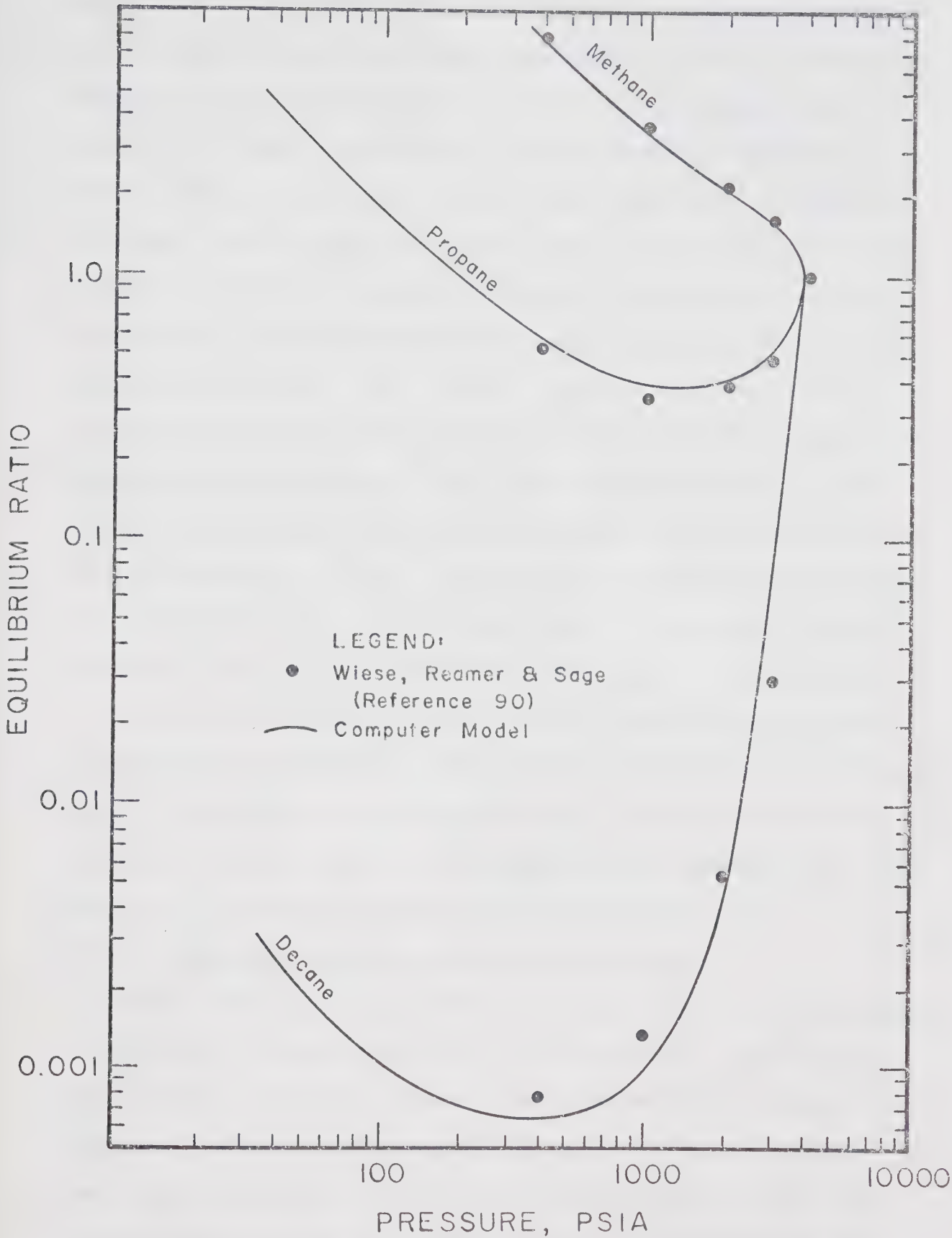
Figure 6-7. Comparison of Calculated and Literature Equilibrium Ratios for the Methane-Propane-Decane Mixtures of Table 6-6.

comparison between the calculated K-values and the experimental K-values interpolated from reference 90 using composition parameters calculated from the liquid phase compositions of Table 6-6. There was generally good agreement between K-values except for decane at 3000 psia, where the calculated value was 0.0678 compared to the experimental value of 0.03. This large error was caused by smaller percentage errors in the K-values calculated from the Chao-Seader correlation at the lower pressures. The smaller errors were magnified by the interpolation formula (Equation 4-12) used to extend the Chao-Seader correlation to the convergence pressure. Relatively large errors were also detected in the decane K-values for the example at 280°F. These errors could also be traced to systematic errors in the Chao-Seader correlation, particularly in the pressure range from 1200 psia to 2000 psia.

The loci of the calculated phase compositions for the two depletion performance calculations are presented in Figure 6-8. It should be noted that the vapor phase compositions vary only slightly whereas the liquid phase compositions vary widely and tend toward pure decane at low pressures.

6.3 (d) Methane, n-Butane and Decane Mixtures

Phase equilibria data have been reported for the methane, n-butane and decane system at 160°F by Reamer, Fiskin and Sage[91] and at 280°F by Reamer, Sage and Lacey[92]. Example depletion performance calculations were performed for the same initial mixture (0.90 mole fraction methane, 0.06 mole fraction n-butane and 0.04 mole fraction decane) at temperatures of 160°F and 280°F. The computer printout for the
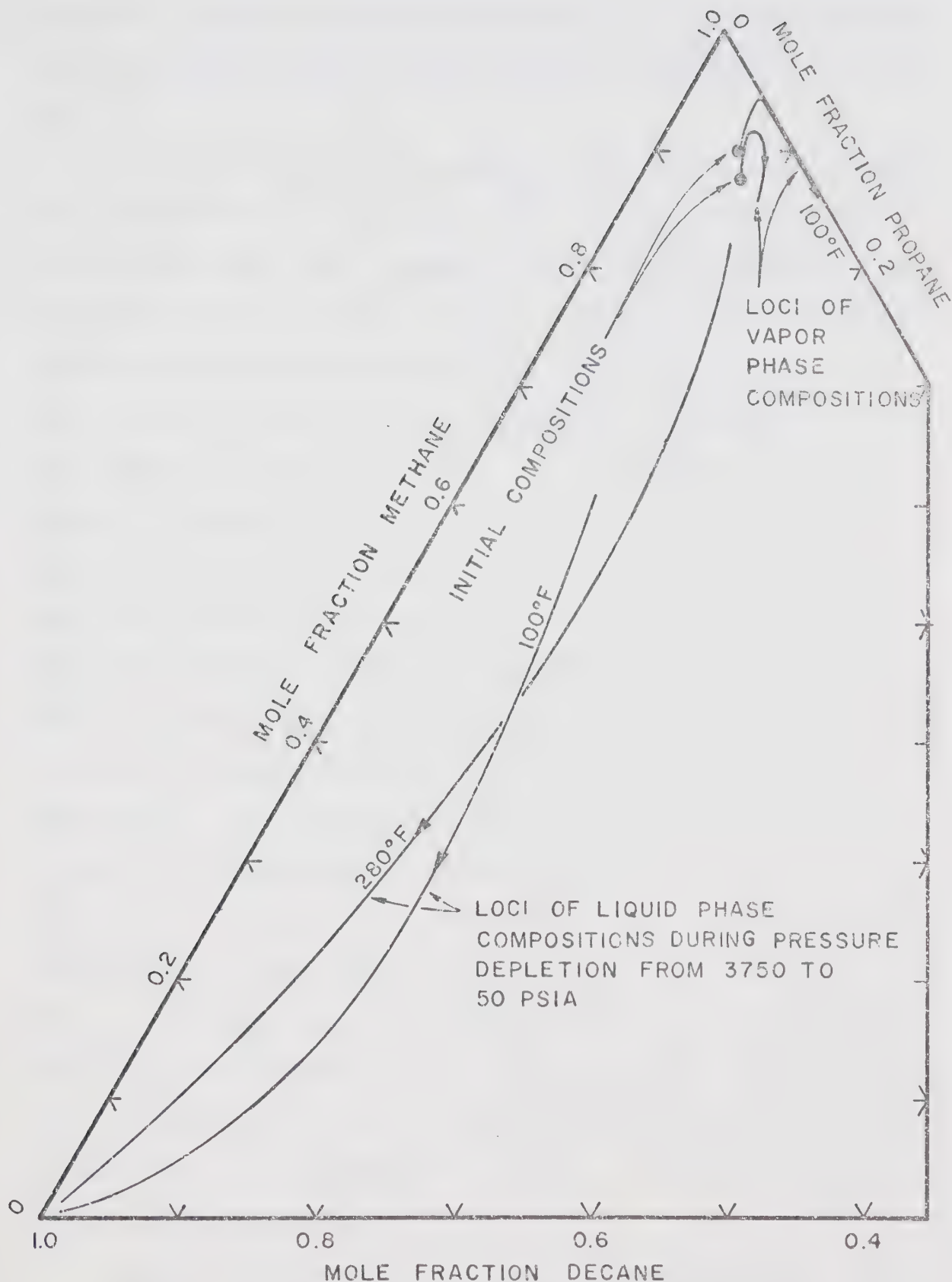
Figure 6-8.  Loci of Phase Compositions for the Simulated
Depletion Performance of the Mixtures given
in Tables 6-6 and E-14.

example at 160°F is presented in Table 6-7, and the printout for the example at 280°F may be found in Table E-15 of Appendix E.

The data of Table 6-7 indicate the retrograde dew point to be approximately 3600 psia. The calculated convergence pressure was 3989 psia compared to an interpolated value of some 4100 psia from reference 91. A comparison of calculated K-values with the experimental data from reference 91 is shown in Figure 6-9. There is remarkable agreement for methane, however, there are systematic discrepancies in the n-butane and decane K-values. The Chao-Seader K-values for decane start to diverge from the experimental data at pressures above about 800 psia. Since the interpolation procedure used Chao-Seader K-values at pressures of 0.1 $P_k$, 0.3 $P_k$ and 0.5 $P_k$ (399, 1197 and 1995 psia, respectively), the errors in the low pressure K-values are carried into the high pressure region. The changeover point (0.5 $P_k$) from Chao-Seader K-values to interpolated K-values for decane is obvious in Figure 6-9. The dashed line shows the locus of the interpolation formula for a short interval below the changeover point. It is apparent that better results would have been obtained if the decane K-values at pressures corresponding to 0.05 $P_k$, 0.1 $P_k$ and 0.2 $P_k$ had been used to develop the coefficients for the interpolation formula. The example at 280°F showed similar behavior.

The loci of the calculated phase compositions for the two examples are shown in Figure 6-10. As expected, an increase in temperature caused the decane content of the vapor

## TABLE 6-7.

METHANE, N-BUTANE, AND N-DECANE MIXTURE AT 160 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

```
------------------------- PURE COMPONENT DATA -------------------------
```

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C4 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 0.195 | 6.770 |
| C10 | 142.276 | 304.0 | 9.660 | 1111.70 | 0.246 | 0.486 | 8.180 |

```
---------------- SIMULATED DEPLETION PERFORMANCE ----------------
```

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.900 | 0.904 | 0.663 | 1.3645 | 3500. | 2.24 | 0.070 | 0.0377 |
| C4 | 0.060 | 0.058 | 0.122 | 0.4807 | | | | |
| C10 | 0.040 | 0.036 | 0.214 | 0.1696 | | | | |
| MOLES | 0.614 | 0.602 | 0.012 | | 3989. | | | |
| C1 | 0.899 | 0.917 | 0.618 | 1.4825 | 3250. | 6.72 | 0.079 | 0.0355 |
| C4 | 0.060 | 0.055 | 0.130 | 0.4264 | | | | |
| C10 | 0.040 | 0.027 | 0.251 | 0.1077 | | | | |
| MOLES | 0.571 | 0.535 | 0.035 | | 3989. | | | |
| C1 | 0.898 | 0.927 | 0.580 | 1.5985 | 3000. | 9.25 | 0.090 | 0.0340 |
| C4 | 0.060 | 0.053 | 0.138 | 0.3855 | | | | |
| C10 | 0.040 | 0.019 | 0.281 | 0.0683 | | | | |
| MOLES | 0.528 | 0.481 | 0.047 | | 3989. | | | |
| C1 | 0.896 | 0.935 | 0.544 | 1.7181 | 2750. | 10.67 | 0.103 | 0.0328 |
| C4 | 0.060 | 0.051 | 0.145 | 0.3529 | | | | |
| C10 | 0.042 | 0.013 | 0.309 | 0.0419 | | | | |
| MOLES | 0.486 | 0.433 | 0.053 | | 3988. | | | |
| C1 | 0.892 | 0.941 | 0.508 | 1.8502 | 2500. | 11.37 | 0.118 | 0.0318 |
| C4 | 0.061 | 0.050 | 0.153 | 0.3259 | | | | |
| C10 | 0.045 | 0.008 | 0.337 | 0.0243 | | | | |
| MOLES | 0.445 | 0.390 | 0.054 | | 3988. | | | |
| C1 | 0.888 | 0.946 | 0.472 | 2.0033 | 2250. | 11.58 | 0.135 | 0.0309 |
| C4 | 0.062 | 0.049 | 0.161 | 0.3036 | | | | |
| C10 | 0.048 | 0.004 | 0.366 | 0.0129 | | | | |
| MOLES | 0.402 | 0.348 | 0.054 | | 3988. | | | |

## TABLE 6-7. (CONT.)

METHANE, N-BUTANE, AND N-DECANE MIXTURE AT 160 F.

```
---------------- SIMULATED DEPLETION PERFORMANCE ----------------
```

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|--------|--------|--------|--------|--------|--------|--------|--------|
| C1  | 0.882 | 0.949 | 0.433 | 2.1889 | 2000. | 11.46 | 0.156 | 0.0300 |
| C4  | 0.064 | 0.048 | 0.170 | 0.2852 | | | | |
| C10 | 0.053 | 0.002 | 0.396 | 0.0061 | | | | |
| MOLES | 0.360 | 0.308 | 0.052 | | 3988. | | | |
| C1  | 0.874 | 0.948 | 0.391 | 2.4229 | 1750. | 10.90 | 0.179 | 0.0291 |
| C4  | 0.066 | 0.048 | 0.179 | 0.2720 | | | | |
| C10 | 0.059 | 0.002 | 0.429 | 0.0055 | | | | |
| MOLES | 0.317 | 0.269 | 0.048 | | 3988. | | | |
| C1  | 0.864 | 0.948 | 0.346 | 2.7361 | 1500. | 10.38 | 0.212 | 0.0282 |
| C4  | 0.068 | 0.049 | 0.187 | 0.2616 | | | | |
| C10 | 0.067 | 0.002 | 0.465 | 0.0048 | | | | |
| MOLES | 0.274 | 0.229 | 0.044 | | 3988. | | | |
| C1  | 0.851 | 0.948 | 0.298 | 3.1767 | 1250. | 9.89 | 0.258 | 0.0274 |
| C4  | 0.071 | 0.049 | 0.194 | 0.2563 | | | | |
| C10 | 0.077 | 0.002 | 0.506 | 0.0040 | | | | |
| MOLES | 0.230 | 0.189 | 0.040 | | 3987. | | | |
| C1  | 0.832 | 0.946 | 0.246 | 3.8413 | 1000. | 9.37 | 0.327 | 0.0265 |
| C4  | 0.075 | 0.051 | 0.199 | 0.2595 | | | | |
| C10 | 0.091 | 0.001 | 0.554 | 0.0034 | | | | |
| MOLES | 0.187 | 0.149 | 0.037 | | 3983. | | | |
| C1  | 0.806 | 0.943 | 0.201 | 4.6760 | 800. | 8.97 | 0.414 | 0.0258 |
| C4  | 0.081 | 0.054 | 0.199 | 0.2729 | | | | |
| C10 | 0.112 | 0.001 | 0.599 | 0.0029 | | | | |
| MOLES | 0.153 | 0.118 | 0.034 | | 3974. | | | |
| C1  | 0.775 | 0.939 | 0.154 | 6.0737 | 600. | 8.52 | 0.555 | 0.0251 |
| C4  | 0.087 | 0.059 | 0.193 | 0.3053 | | | | |
| C10 | 0.137 | 0.001 | 0.651 | 0.0027 | | | | |
| MOLES | 0.119 | 0.087 | 0.031 | | 3951. | | | |
| C1  | 0.730 | 0.935 | 0.129 | 7.1950 | 500. | 8.30 | 0.666 | 0.0247 |
| C4  | 0.094 | 0.063 | 0.188 | 0.3353 | | | | |
| C10 | 0.174 | 0.001 | 0.681 | 0.0026 | | | | |
| MOLES | 0.103 | 0.072 | 0.030 | | 3929. | | | |

TABLE 6-7.    (CONT.)

METHANE, N-BUTANE, AND N-DECANE MIXTURE AT 160 F.

------------ SIMULATED DEPLETION PERFORMANCE ------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.697 | 0.929 | 0.104 | 8.8810 | 400. | 8.06 | 0.829 | 0.0244 |
| C4 | 0.100 | 0.068 | 0.179 | 0.3835 | | | | |
| C10 | 0.202 | 0.001 | 0.715 | 0.0027 | | | | |
| MOLES | 0.086 | 0.057 | 0.028 | | 3892. | | | |
| C1 | 0.653 | 0.919 | 0.078 | 11.6986 | 300. | 7.81 | 1.093 | 0.0240 |
| C4 | 0.105 | 0.077 | 0.166 | 0.4676 | | | | |
| C10 | 0.240 | 0.002 | 0.754 | 0.0029 | | | | |
| MOLES | 0.070 | 0.043 | 0.027 | | 3832. | | | |
| C1 | 0.592 | 0.903 | 0.052 | 17.3517 | 200. | 7.52 | 1.596 | 0.0236 |
| C4 | 0.112 | 0.093 | 0.145 | 0.6411 | | | | |
| C10 | 0.295 | 0.002 | 0.802 | 0.0035 | | | | |
| MOLES | 0.054 | 0.028 | 0.025 | | 3719. | | | |
| C1 | 0.499 | 0.889 | 0.038 | 23.0153 | 150. | 7.37 | 2.071 | 0.0234 |
| C4 | 0.118 | 0.107 | 0.131 | 0.8172 | | | | |
| C10 | 0.382 | 0.003 | 0.830 | 0.0042 | | | | |
| MOLES | 0.046 | 0.021 | 0.024 | | 3613. | | | |
| C1 | 0.430 | 0.865 | 0.025 | 34.3675 | 100. | 7.19 | 2.964 | 0.0231 |
| C4 | 0.120 | 0.129 | 0.110 | 1.1717 | | | | |
| C10 | 0.449 | 0.004 | 0.863 | 0.0056 | | | | |
| MOLES | 0.038 | 0.014 | 0.023 | | 3435. | | | |
| C1 | 0.337 | 0.815 | 0.011 | 68.5303 | 50. | 6.95 | 5.364 | 0.0229 |
| C4 | 0.117 | 0.175 | 0.078 | 2.2396 | | | | |
| C10 | 0.544 | 0.009 | 0.909 | 0.0099 | | | | |
| MOLES | 0.029 | 0.007 | 0.022 | | 3076. | | | |
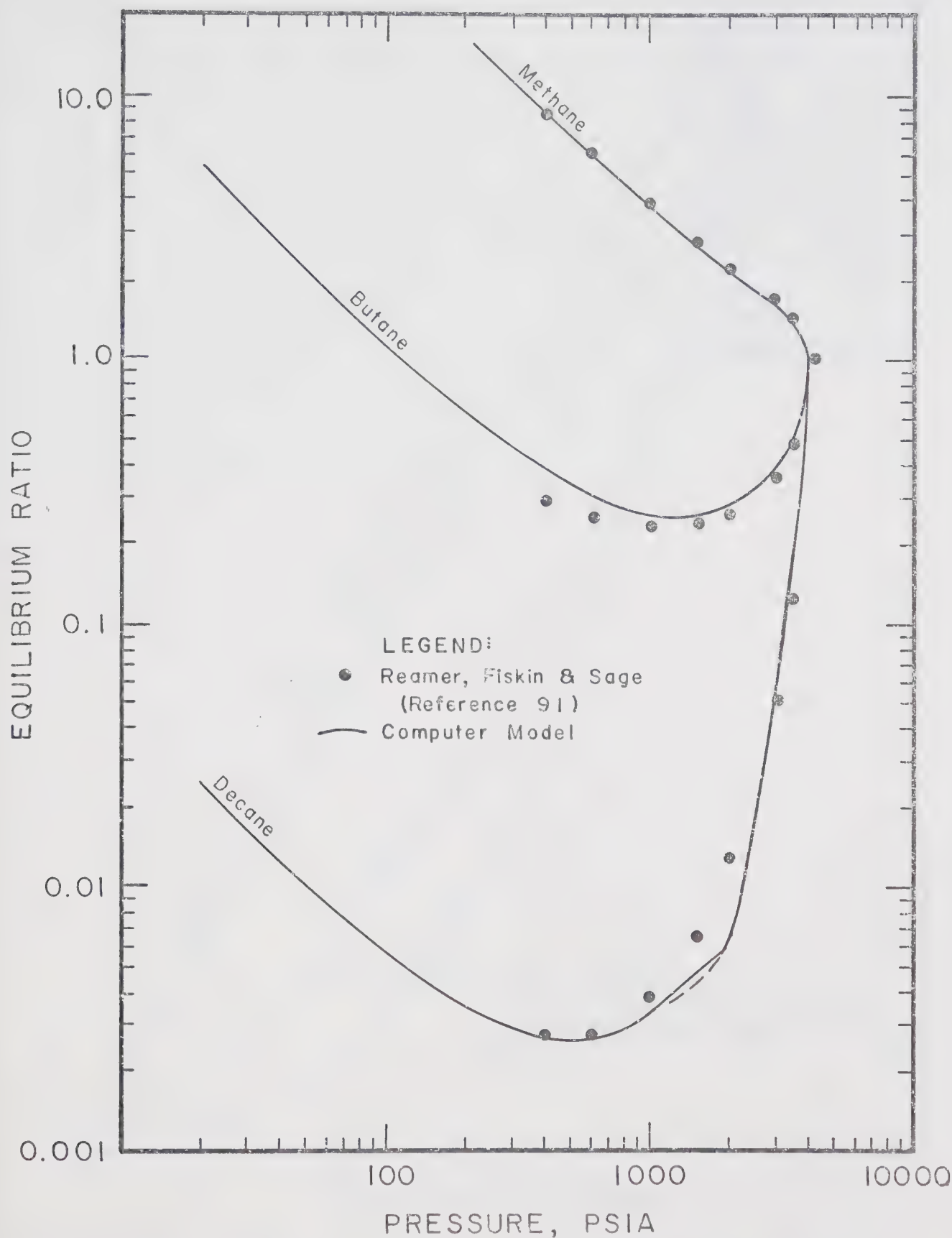
Figure 6-9.  Comparison of Calculated and Literature Equilib-
rium Ratios for the Methane-n-Butane-Decane
Mixtures of Table 6-7.
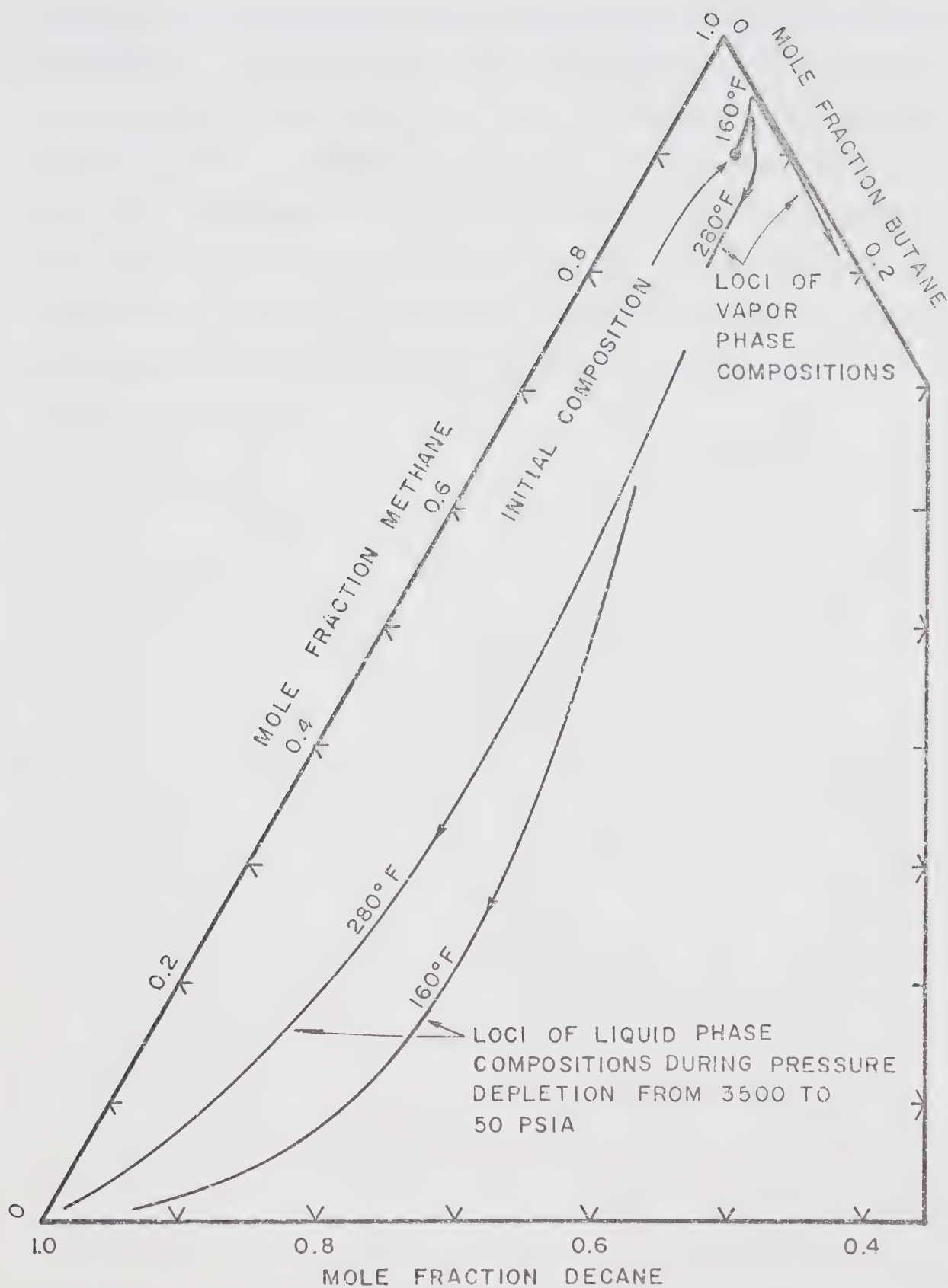
Figure 6-10.  Loci of Phase Compositions for the Simulated
Depletion Performance of the Mixtures given
in Tables 6-7 and E-15.

phase to increase and the decane content of the liquid phase
to decrease. The volume per cent retrograde liquid for the
two examples is shown in Figure 6-11. The effect of increased
temperature was to decrease the amount of retrograde liquid.
There is a discrepancy in the calculated dew points inasmuch
as the dew point at 280°F is indicated to be some 200 psi
higher than at 160°F. This type of discrepancy might have
been expected in view of the difficulties in extrapolating
the decane K-values.
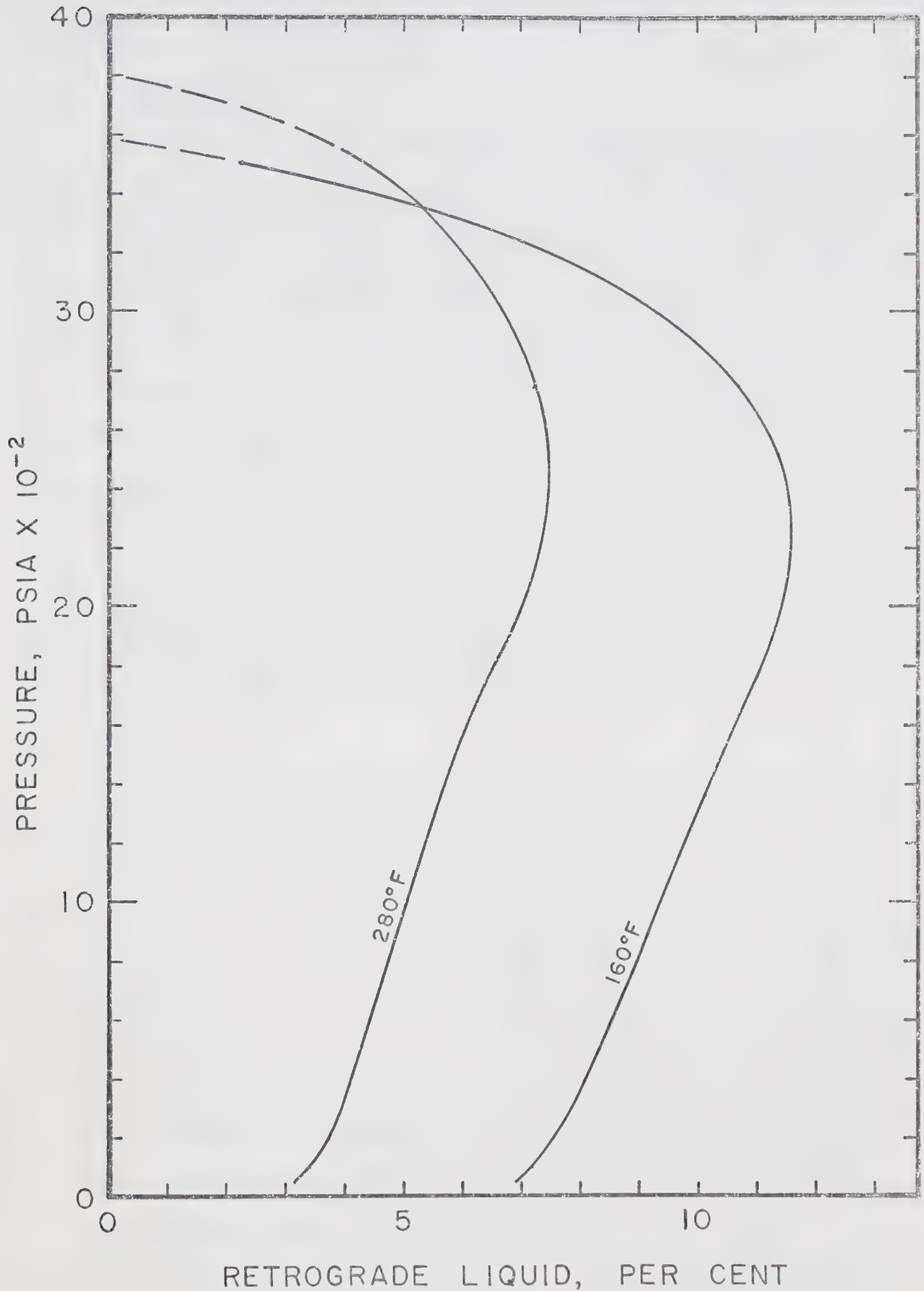
Figure 6-11.  Volume Per Cent Retrograde Liquid for the
Example Depletion Calculations Presented
in Tables 6-7 and E-15.

Chapter 7.   CONCLUSIONS AND RECOMMENDATIONS

7.1   Conclusions

The object of the experimental work was to design and
construct an apparatus to study some of the effects that po-
rous media have on the phase behavior of retrograde hydrocar-
bon mixtures.  Except for some initial shakedown runs, the
experimental work was directed toward obtaining photographs
of retrograde liquid capillary structures in packs of uniform
spheres.  The photographs were used in a theoretical study of
the effect of interface curvature on phase behavior carried
out by the Petroleum Recovery Research Institute of Calgary.
That study indicated that the curvature of the vapor-liquid
interface would have a negligible effect on phase equilibrium
except in a porous medium with a grain diameter  of a few
microns.

The conclusions with regard to the experimental aspect
of this work are qualitative and generally pertain to the
apparatus.  The work concerning the calculation procedure
developed to approximate the pressure depletion of retrograde
hydrocarbon mixtures was carried on independently of the
experimental program.  Conclusions concerning this phase of
the work are based on the results presented in this thesis.

1.  The air bath enclosure proved to be a convenient means
    of maintaining good temperature control for the bulky
    equipment used in this study.

2.  The general procedure for determining bubble or dew
    point pressures by using a differential pressure

transducer is believed to be an original innovation. The procedure may have some application in conventional PVT work.

3. The data of this work indicates that during the isothermal depletion of binary retrograde hydrocarbon mixtures, equilibrium between phases is spontaneous over the pressure interval that liquids are condensing.

4. The data of this work indicates that mass transfer from the liquid phase to the vapor phase in the packed cell did not appear to be enhanced by the forced convection of the vapor phase.

5. An explanation was developed for the tendency toward non-equilibrium between coexisting phases over the pressure interval that retrograde liquids vaporize. It was shown that the variation of phase fugacity with composition was important in this regard.

6. A new equation of state procedure was developed for the analytical representation of isochores. The method was demonstrated by applying it to the corresponding states correlation of Lydersen, Greenkorn and Hougen.

7. A calculation procedure was developed to extrapolate K-values from the Chao-Seader correlation over the high pressure region to the convergence pressure defined by the critical composition method.

8. The widely used Standing and Katz correlation was found to exhibit anomalous behavior along the isotherms $T_r =$ 1.05, 1.10 and 1.15. This behavior could be due to poor data or due to the failure of Kay's rule to correlate

the data in this region.

9. The BWR equation of state was found to give a good representation of the vapor region for various corresponding states compressibility factor correlations.

10. The Redlich-Kwong equation was found to give the best two-parameter equation of state approximation for the isochores of the reduced correlation by Rowlinson.

11. The work summarized in Appendix F shows that true $Z_c$ factors for binary mixtures have significant and systematic departures from the mole averages of the pure component $Z_c$ values.

## 7.2 Recommendations

1. Any future experimental program should use much smaller diameter glass beads (200 microns or less) in the packed cell. The smaller beads will prevent gravity segregation of liquids within the pack and should eliminate much of the anomalous non-equilibrium data.

2. Large cylinders of retrograde mixtures should be prepared and stored at pressures above their dew points. These cylinders could be used to obtain identical charges for experiments to determine the effects of rate, bead size and temperature on vaporization of retrograde liquids.

3. The mercury manometer for the gas density balance was a major cause of experimental difficulty and it should be replaced before an extensive experimental program is undertaken. A high precision pressure transducer or a quartz Bourdon tube could be used in place of the manometer.

4. The generalized equation of state procedure developed in this work should be applied to the raw data for some pure components which are known to be of high accuracy. This may involve development of temperature-explicit or pressure-explicit equations for the saturated state.

5. An improved procedure should be developed to insure that the upper pressure limit of the Chao-Seader correlation is never exceeded. This is particularly important for the points used to evaluate the coefficients in the extrapolation formula.

6. The accuracy of the phase density calculations should be improved. This might be achieved by using a more complex mixing rule to calculate pseudocritical temperature. The minimization of density errors is important since density is used to calculate the system composition for the next flash. Errors at any flash are carried forward and can accumulate to a significant amount.

7. The phase simulation program developed in this work should be modified so that it can be applied to more than three components. This would require a different search procedure for the mixture having a critical temperature equal to the system temperature.

NOMENCLATURE

A, B, C, D,
E, F, G, H   = functions of specified arguments or coefficients depending upon usage

K            = equilibrium ratio or K-value

P            = pressure

$P_k$        = convergence pressure

R            = universal gas constant

T            = temperature

V            = volume

X            = dummy variable

Z            = compressibility factor

a, b         = coefficients in a two-parameter equation of state

f            = fugacity

k            = constant in Equation 5-4

ln           = natural logarithm

log          = logarithm, base other than e

n            = integer limit

v            = partial molar volume

x            = mole fraction in a liquid solution

y            = mole fraction in a vapor mixture


Greek Letters

$\alpha$     = Riedel factor

$\gamma$     = activity coefficient

$\delta$     = solubility parameter

$\delta_c$   = parameter to characterize the orientational forces between molecules

$\varepsilon$ = small value used as a convergence criterion

$\nu$ = fugacity coefficient in the liquid solution

$\rho$ = density

$\phi$ = fugacity coefficient in the vapor mixture

$\omega$ = acentric factor

Subscripts

c = value at the critical state

i, j, m, n = integer indices

L = liquid phase property

p = pseudo property

r = reduced value of the variable

s = value of the variable at saturation

V = vapor phase property

standard error = $\sqrt{\dfrac{1}{n} \displaystyle\sum_{i=1}^{n} \left( \dfrac{X_{data} - X_{calc}}{X_{data}} \right)^2}$

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APPENDIX A

LEAST SQUARES FITTING TECHNIQUES

## A.1 Foreword

Several attempts were made to obtain suitable approxima-
tions for the various corresponding states correlations.  In-
itially compressibility factors were approximated by power
polynomials in reduced pressure and reduced temperature.  The
usual problem of the least squares normal equations forming
an ill-conditioned matrix was avoided by using orthogonal
polynomials.  However, orthogonal polynomials had the disad-
vantage that values of the dependent variable were required
at every point in the rectangular grid covered by the values
selected for the independent variables.  This disadvantage
did not present any problem when reduced pressure and reduced
temperature were used as independent variables since the cor-
relations are normally tabulated in this fashion.  The prob-
lem was that functional forms which used reduced temperature
and reduced pressure were not very satisfactory for approxi-
mating the correlations.

The next attempt at approximating the correlations used
power polynomials in reduced temperature and reduced density.
These functions resulted in better approximations but orthog-
onal polynomials could not be used unless the data was
plotted and extrapolated so that the dependent variable was
known at every point in the grid formed by the independent
variables.  At this point linear programming was considered.
This method was soon rejected because if the functional form
was satisfactory it was tantamount to basing the approxima-
tion on the poorest data points (extreme points) in the cor-
relation.

Finally, it was decided to attempt to use some of the well-known equations of state. These equations are usually non-linear with respect to their parameters. The parameters for non-linear equations can be conveniently estimated by an algorithm proposed by Marquardt[77] provided that the matrix that forms the normal equations is not ill-conditioned. This restriction has the effect of limiting the number of parameters to about twelve.

## A.3 Computer Program

A listing of the FORTRAN program used to fit the Standing and Katz correlation to a reduced form of the B-W-R equation is reproduced on pages A-3 to A-9. The main program reads the data, calculates the matrix for the normal equations, uses Marquardt's algorithm to improve the current estimates for the least squares parameters, and controls the print out of the report. The reduced form of the B-W-R equation was specified in a function subprogram. The program could be adapted to other equations of state simply by changing the function subprogram and the statements containing the partial derivatives with respect to the least squares parameters.

The inverse of the matrix was calculated by two subroutines. Subroutine PARTN partitioned the matrix into upper and lower triangular matrices. Subroutine INVER calculated the inverses of the triangular matrices and multiplied them together to obtain the inverse matrix. This method of direct inversion may be subject to round-off error. A test was made to see if round-off was significant and, if necessary, subroutine IMPRO was used to improve the inverse matrix.

```
      IMPLICIT REAL*8 (A-H, O-Z)
      DIMENSION R(75), FL(75,20), TR(20), PL(40),  PR(75),
     1 DF(10), D(10,10), U(10,10), ALHS(10,10), B(10), A(10), RHS(10),
     2 C(10), X(10),X1(75)
      COMMON ALHS, C, U
    1 FORMAT(20F4.3)
    2 FORMAT(1X,6E20.8)
    3 FORMAT(' ')
    4 FORMAT(1X,F5.2,1X,20F5.1)
    5 FORMAT(1X,I6)
    6 FORMAT(7X,20F5.2,/)
    7 FORMAT('1'/)
    8 FORMAT('0CAUTION IMPROV USED 10 ITERATIONS')
    9 FORMAT('0APPROXIMATION OF STANDING-KATZ CORRELATION WITH RNR'/)
      M=8
      AN=4
      N=0
      S=0.0
      IC=75
      LL=20
      READ(5,1)W1
      READ(5,1)(TR(L),L=1,LL)
      READ(5,1)(PR(I),I=1,IC)
      DO 20 I=1,IC
      READ(5,1)(F2(I,L),L=1,LL)
      DO 19 L=1,LL
      IF(F2(I,L))19,19,18
   18 N=N+1
      S=S+F2(I,L)
   19 CONTINUE
   20 CONTINUE
      AN=N
      WRITE(6,2)S
      WRITE(6,5)N
      DO 95 INT=2,3
      WRITE(6,7)
      A(1)=0.1743
      A(2)=-0.609
      A(3)=-0.91
      A(4)=0.655
      A(5)=-0.76
      A(6)=-0.081
      A(7)=0.985
      A(8)=0.58
      A(9)=1.0
      A(10)=1.0
      DO 70 ITER=1,11
      VAR1=0.0
      VAR2=0.0
      DO 21 I=1,M
      C(I)=A(I)
      B(I)=0.0
      RHS(I)=0.0
      DO 21 J=1,M
      ALHS(I,J)=0.0
```

```
 21 CONTINUE
    DO 40 I=1,IE
    DO 40 L=1,LL
    W=1.0
    IF(L.EQ.1)W=W1(I)
    IF(L.EQ.2)W=W1(I)
    IF(L.EQ.3)W=2.0
    IF(L.EQ.16)W=2.0
    IF(L.EQ.19)W=5.0
    IF(L.EQ.20)W=10.0
    R(I)=RP(I)*0.270/(F2(I,L)*TR(L))
 32 F=FCALC(R(I),TR(L),A(1),A(2),A(3),A(4),A(5),A(6),A(7),A(8),A(9),
   1 A(10))
    R2=R(I)**2
    DF(1)=R(I)
    DF(2)=R(I)/TR(L)
    DF(3)=R(I)/TR(L)**3
    DF(4)=R2
    DF(5)=R2/TR(L)+A(6)*R(I)**5/TR(L)
    DF(6)=A(5)*R(I)**5/TR(L)
    DF(7)=R2/TR(L)**3*(1.0+A(8)*R2)*DEXP(-A(8)*R2)
    DF(8)=-A(7)*A(8)*R(I)**6/TR(L)**3*DEXP(-A(8)*R2)
    VAR1=VAR1+(F2(I,L)-F)**2*W
    VAR2=VAR2+(1.0-F/F2(I,L))**2*W
    DO 25 J=1,M
    IF(IWT-2)22,23,24
 22 RHS(J)=RHS(J)+(F2(I,L)-F)*DF(J)
    GO TO 25
 23 RHS(J)=RHS(J)+(F2(I,L)-F)*DF(J)/F2(I,L)**2*W
    GO TO 25
 24 RHS(J)=RHS(J)+(F2(I,L)-F)*DF(J)*W
 25 CONTINUE
    DO 33 K=1,M
    IF(IWT-2)26,27,28
 26 ALHS(J,K)=ALHS(J,K)+DF(J)*DF(K)
    GO TO 29
 27 ALHS(J,K)=ALHS(J,K)+DF(J)*DF(K)/F2(I,L)**2*W
    GO TO 29
 28 ALHS(J,K)=ALHS(J,K)+DF(J)*DF(K)*W
 29 CONTINUE
 33 CONTINUE
 40 CONTINUE
    IF(ITER-1)34,34,35
 34 ALAM=0.01
 35 DO 36 I=1,M
    B(I)=ALHS(I,I)
 36 CONTINUE
    RMS1=DSQRT(VAR1/AN)
    RMS2=DSQRT(VAR2/AN)
    WRITE(6,2)(A(J),J=1,M),RMS1,RMS2
    WRITE(6,3)
 41 DO 42 I=1,M
    ALHS(I,I)=B(I)+ALAM
 42 CONTINUE
    CALL PARIN(M)
```

```
      CALL INVER(M)
      CALL INPRO(M,KEY)
      IF(KEY)84,84,83
83    WRITE(6,3)
84    ICODE=0
      DO 51 J=1,M
      E(J)=0.0
      DO 50 K=1,M
      E(J)=E(J)+D(J,K)*CB(K)
50    CONTINUE
      A(J)=C(J)+E(J)
      TEST=ABS(E(J))/(0.001+ABS(C(J)))
      IF(TEST-0.000005)51,51,55
55    ICODE=1
51    CONTINUE
      IF(ICODE)52,50,52
52    RMS1=0.0
      RMS2=0.0
      DO 44 I=1,IE
      DO 44 L=1,LL
      W=1.0
      IF(L.EQ.1)W=W1(I)
      IF(L.EQ.2)W=W1(I)
      IF(L.EQ.5)W=2.0
      IF(L.EQ.10)W=2.0
      IF(L.EQ.15)W=5.0
      IF(L.EQ.20)W=1.0
      R(I)=PR(I)*0.270/(F2(I,L)*TR(L))
      F=FCALC(R(I),TR(L),A(1),A(2),A(3),A(4),A(5),A(6),A(7),A(8),A(9),
     1 A(10))
      RMS1=RMS1+(F2(I,L)-F)**2*W
      RMS2=RMS2+(1.0-F/F2(I,L))**2*W
44    CONTINUE
      WRITE(6,2)ALAM,RMS1,VAR1,RMS2,VAR2
      IF(INT-2)45,46,45
45    IF(RMS1-VAR1)45,45,49
46    IF(RMS2-VAR2)45,45,49
45    ALAM=ALAM/10.0
      GO TO 47
49    ALAM=ALAM*10.0
      GO TO 41
47    WRITE(6,3)
70    CONTINUE
80    CONTINUE
      VAR1=0.0
      VAR2=0.0
      LS=1
      LE=20
      WRITE(6,7)
      WRITE(6,9)
      WRITE(6,6)(TR(L),L=LS,LE)
      DO 93 I=1,IE
      DO 92 L=LS,LE
      PE(L)=0.0
      R(I)=PR(I)*0.270/(F2(I,L)*TR(L))
```

```
      F=FCALC(R(I),TR(L),A(1),A(2),A(3),A(4),A(5),A(6),A(7),A(8),A(9),
     1 A(10))
      VAR1=VAR1+(F2(I,L)-F)**2
      VAR2=VAR2+(1.0-F/F2(I,L))**2
      PE(L)=100.0*(1.0-F/F2(I,L))
   92 CONTINUE
      WRITE(6,4)PR(I),(PE(L),L=LS,LL)
   95 CONTINUE
      WRITE(6,5)
      RMS1=DSQRT(VAR1/AN)
      RMS2=DSQRT(VAR2/AN)
      WRITE(6,2)RMS1,RMS2
   95 CONTINUE
      STOP
      END




      DOUBLE PRECISION FUNCTION FCALC(R,T,A1,A2,A3,A4,A5,A6,A7,A8,A9,A10
     1)
      IMPLICIT REAL*8(A-F,O-Z)
      R2=R*R
      FCALC=1.0+(A1+A2/T+A3/T**3)*R+(A4+A5/T)*R2+A6*R6*R**5/T+
     1 A7*R2/T**3*(1.0+A8*R2)*DEXP(-A8*R2)
      RETURN
      END
```

```
      SUBROUTINE PARTN(N)
      DOUBLE PRECISION A(10,10), D(10,10), U(10,10)
      COMMON A, D, U
      INTEGER I, J, K, N, KP1, KM1
      DO 1 I=1,N
      DO 1 J=1,N
      D(I,J)=0.0
      U(I,J)=0.0
    1 CONTINUE
C     DETERMINE D AND U TRIANGULAR MATRICES SUCH THAT A=D*U
      D(1,1)=1.0
      U(1,1)=A(1,1)
      DO 2 J=2,N
      U(1,J)=A(1,J)
      D(J,1)=A(J,1)/U(1,1)
    2 CONTINUE
      DO 7 K=2,N
      KM1=K-1
      KP1=K+1
      DO 3 J=K,N
      U(K,J)=A(K,J)
      DO 3 I=1,KM1
      U(K,J)=U(K,J)-D(K,I)*U(I,J)
    3 CONTINUE
      D(K,K)=1.0
      IF(KP1-N)4,4,7
    4 DO 6 I=KP1,N
      D(I,K)=A(I,K)
      DO 5 J=1,KM1
      D(I,K)=D(I,K)-U(J,K)*D(I,J)
    5 CONTINUE
      D(I,K)=D(I,K)/U(K,K)
    6 CONTINUE
    7 CONTINUE
      RETURN
      END
```

```fortran
      SUBROUTINE INVER(N)
      DOUBLE PRECISION A(10,10), D(10,10), U(10,10), P(10,10), Q(10,10)
      COMMON A, D, U
      INTEGER I, J, K, N, IM1, IP1, JM1, IR
      DO 2 I=1,N
      DO 1 J=1,N
      P(I,J)=0.0
      Q(I,J)=0.0
    1 CONTINUE
      P(I,I)=1.0/U(I,I)
      Q(I,I)=1.0/D(I,I)
    2 CONTINUE
C     CALCULATE P, THE INVERSE OF U
      DO 4 J=2,N
      JM1=J-1
      DO 4 K=1,JM1
      I=J-K
      IP1=I+1
      DO 3 IR=IP1,J
      P(I,J)=P(I,J)+U(I,IR)*P(IR,J)
    3 CONTINUE
      P(I,J)=-P(I,J)/U(I,I)
    4 CONTINUE
C     CALCULATE Q, THE INVERSE OF D
      DO 6 I=2,N
      IM1=I-1
      DO 6 K=1,IM1
      J=I-K
      DO 5 IR=J,IM1
      Q(I,J)=Q(I,J)+D(I,IR)*Q(IR,J)
    5 CONTINUE
      Q(I,J)=-Q(I,J)/D(I,I)
    6 CONTINUE
C     MULTIPLY P*Q TO OBTAIN INVERSE OF A
      DO 7 I=1,N
      DO 7 J=1,N
      D(I,J)=0.0
      DO 7 K=1,N
      D(I,J)=D(I,J)+P(I,K)*Q(K,J)
    7 CONTINUE
      RETURN
      END
```

```fortran
      SUBROUTINE IMPRO(N,KEY)
      DOUBLE PRECISION A(10,10), D(10,10), U(10,10), ERR, MAX
      COMMON A, D, U
      INTEGER I, J, K, L, N, KEY
      KEY=0
      DO 6 L=1,10
      MAX=0.0D0
      DO 1 I=1,N
      DO 1 J=1,N
      U(I,J)=0.0D0
      DO 1 K=1,N
      U(I,J)=U(I,J)+A(I,K)*U(K,J)
    1 CONTINUE
      DO 3 I=1,N
      U(I,I)=U(I,I)-1.0D0
      DO 3 J=1,N
      IF(DABS(U(I,J))-MAX)3,3,2
    2 MAX=DABS(U(I,J))
    3 CONTINUE
      IF(MAX-1.0D-6)7,7,4
    4 DO 6 I=1,N
      DO 6 J=1,N
      ERR=0.0D0
      DO 5 K=1,N
      ERR=ERR+D(I,K)*U(K,J)
    5 CONTINUE
      D(I,J)=D(I,J)-ERR
    6 CONTINUE
      KEY=1
    7 RETURN
      END
```

APPENDIX B

TWO-PARAMETER EQUATIONS OF STATE

## B.1   Foreword

Some of the classical two-parameter equations of state are reviewed in this appendix. Particular attention was given to the functional forms these equations have for approximating isochores. The objective of this investigation was to gain some insight as to what functions might be appropriate for approximating the reduced isochores of various corresponding states density correlations. A test of the suitability of each equation was made by fitting the reduced form of the equation to the $ZT_r$ isochores of Rowlinson's correlation.

## B.2   van der Waals Equation

The early work of van der Waals forms the basis of the theorem of corresponding states. Based on kinetic considerations and the fact that on a pressure versus volume plot the critical isotherm has a slope equal to zero, and a point of inflection, at the critical state, van der Waals proposed the equation

$$P + a/V^2 = RT/(V - b) \tag{B-1}$$

The term $a/V^2$ was intended to account for the intermolecular attractive forces (cohesive pressure), and the parameter b was to allow for the volume occupied by the molecules. The two constraints on the critical isotherm at the critical point can be expressed in equation form.

$$(\partial P/\partial V)_T = -RT_c/(V_c - b)^2 + 2a/V_c^3 = 0 \tag{B-2}$$

$$(\partial^2 P/\partial V^2)_T = 2RT_c/(V_c - b)^3 - 6a/V_c^4 = 0 \tag{B-3}$$

Equations B-1, B-2 and B-3 can be solved for the critical

constants with the result

$$P_c = a/(27\ b^2) \qquad V_c = 3\ b \qquad T_c = 8\ a/(27\ bR) \qquad (B-4)$$

These values for the critical constants imply that

$$Z_c = P_c V_c/(R T_c) = 3/8 \qquad (B-5)$$

for all substances. Equations B-4 and B-5 can be used to develop the reduced form of van der Waals equation.

$$P_r + 3/V_r = 8\ T_r/\{3(V_r - 1/3)\} \qquad (B-6)$$

Equation B-6 is a cubic equation in $V_r$ which can be rewritten in terms of the compressibility factor.

$$Z^3 + \left[\frac{P_r}{8\ T_r} + 1\right]Z^2 + \left(\frac{27\ P_r}{64\ T_r^2}\right)Z - \frac{27\ P_r^2}{512\ T_r^3} = 0 \qquad (B-7)$$

Since a cubic equation can be solved explicitly, Equation B-7 illustrates that $Z = f(P_r, T_r)$, which is a statement of the law of corresponding states. This law states that when different substances are subjected to conditions such that they have the same reduced pressure and reduced temperature, they will have the same compressibility factor. An expression similar to Equation B-7 can be developed for every two-parameter equation of state provided it has an algebraic form capable of giving a point of inflection at the critical state.

Even though two-parameter equations of state fail to correctly describe the critical state and dense fluid regions, graphical representations of the relation $Z = f(P_r, T_r)$ have good accuracy. For desk calculations graphical representations are convenient, however, for computer applications an analytical formulation is required. Selection of $P_r$ and $T_r$

for independent variables results in an explicit solution, but a difficult ZPT surface to approximate. When $V_r$ is taken as one of the independent variables the solution becomes implicit, however, the ZVT or ZVP surfaces are not as difficult to approximate.

Two density-implicit formulations are possible for the compressibility factor. Selection of $V_r$ and $P_r$ as independent variables for van der Waals equation results in the following expression

$$Z = 3 P_r V_r^3 / (3 P_r V_r^3 - 9 V_r - P_r V_r^2 + 3) \tag{B-8}$$

When $V_r$ and $T_r$ are selected for independent variables Z can be calculated from the expression

$$Z = V_r / (V_r - 1/3) - 9/(8 T_r V_r) \tag{B-9}$$

Equation B-8 predicts the $P_r/Z$ isochores to have the following form

$$P_r/Z = P_r - 3/V_r^2 - P_r/(3 V_r) + 1/V_r^3 \tag{B-10}$$

Differentiation of Equation B-10 with respect to $P_r$ indicates that van der Waals equation predicts linear isochores with slopes equal to

$$\left( \partial (P_r/Z) / \partial P_r \right)_{V_r} = 1 - 1/(3 V_r) = (V_r - 1/3)/V_r \tag{B-11}$$

A similar development for the $ZT_r$ isochores results in

$$ZT_r = V_r T_r / (V_r - 1/3) - 9/(8 V_r) \tag{B-12}$$

and differentiation with respect to $T_r$ shows these isochores to have slopes which are the reciprocal of the $P_r/Z$ isochores

$$\left( \partial (ZT_r) / \partial T_r \right)_{V_r} = V_r / (V_r - 1/3) \tag{B-13}$$

It should be noted that if $V_r < 1/3$, Equations B-11 and B-13 predict the absurd result that the isochores have a negative slope.

The $ZT_r$ values calculated from Equation B-12 differ from the correlation of Rowlinson by a standard error of 7.81 per cent. As a further test of the suitability of the functional form given by Equation B-12 the two critical state parameters, $a = 9/8$ and $b = 1/3$, were replaced by least squares estimators A and B. After substitution of $\rho_r^{-1}$ for $V_r$, the following equation was fitted to Rowlinson's correlation.

$$ZT_r = T_r/(1 - B\rho_r) - A\rho_r \qquad (B-14)$$

For the 713 points in the reduced density range from 0.05 to 1.0, the standard error was 2.51 per cent, indicating the form to have considerable merit. Table B-1 gives the percentage differences, $100(1 - (ZT_r)_{calc.}/(ZT_r)_{Rowl.})$, for a representative number of points. It should be noted from Table B-1 that the largest errors occur along the critical isotherm.

When Equation B-14 was fitted to 893 points with reduced densities ranging from 0.05 to 1.50, the standard error increased to 5.49 per cent. Table B-2 summarizes the percentage errors for this case.

Tables B-1 and B-2 indicate that the largest differences with van der Waals equation occur as the saturated state is approached. Isochores exhibit the greatest curvature as the saturated state is approached, and since van der Waals equation predicts linear isochores, large errors result.

A summary of the pertinent data for approximations of

## TABLE B-1.

APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.
TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND VAN DER WAALS EQUATION.

| Pr \ Tr | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | -0.5 | -0.3 | -0.1 | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | 0.5 | 0.4 | 0.5 | 0.4 | 0.4 |
| 0.10 | -1.0 | -0.6 | -0.3 | 0.1 | 0.3 | 0.6 | 0.7 | 0.8 | 0.8 | 0.9 | 0.9 | 1.0 | 1.0 | 0.9 | 1.0 | 1.0 | 0.9 |
| 0.15 | -1.5 | -0.9 | -0.5 | 0.2 | 0.6 | 0.9 | 1.1 | 1.2 | 1.3 | 1.4 | 1.4 | 1.5 | 1.5 | 1.4 | 1.4 | 1.3 | 1.3 |
| 0.20 | -2.0 | -1.2 | -0.5 | 0.4 | 1.0 | 1.3 | 1.5 | 1.7 | 1.7 | 1.9 | 1.9 | 2.0 | 2.0 | 1.9 | 1.9 | 1.8 | 1.7 |
| 0.25 | -2.8 | -1.5 | -0.7 | 0.6 | 1.4 | 1.8 | 2.0 | 2.1 | 2.3 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.2 | 2.2 | 2.0 |
| 0.30 | -3.5 | -1.9 | -0.7 | 0.7 | 1.7 | 2.1 | 2.5 | 2.6 | 2.7 | 2.9 | 2.8 | 2.9 | 2.8 | 2.8 | 2.6 | 2.5 | 2.4 |
| 0.35 | -4.1 | -2.4 | -1.0 | 0.9 | 1.9 | 2.5 | 2.8 | 3.1 | 3.2 | 3.2 | 3.3 | 3.3 | 3.4 | 3.1 | 3.0 | 2.8 | 2.6 |
| 0.40 | -4.5 | -2.6 | -1.3 | 1.0 | 2.2 | 2.8 | 3.3 | 3.4 | 3.5 | 3.5 | 3.5 | 3.5 | 3.6 | 3.3 | 3.1 | 3.0 | 2.7 |
| 0.45 | -4.7 | -2.7 | -1.2 | 0.9 | 2.4 | 3.2 | 3.5 | 3.7 | 3.7 | 3.8 | 3.8 | 3.8 | 3.8 | 3.5 | 3.2 | 3.1 | 2.7 |
| 0.50 | -4.9 | -2.8 | -1.2 | 0.9 | 2.3 | 3.2 | 3.6 | 3.9 | 3.8 | 4.0 | 3.9 | 3.9 | 3.8 | 3.5 | 3.3 | 3.0 | 2.6 |
| 0.55 | -4.8 | -2.7 | -1.0 | 1.0 | 2.3 | 3.2 | 3.6 | 3.9 | 3.9 | 3.9 | 3.9 | 4.0 | 3.7 | 3.4 | 3.2 | 3.0 | 2.4 |
| 0.60 | -4.1 | -2.2 | -0.7 | 1.1 | 2.4 | 3.2 | 3.5 | 3.8 | 4.0 | 4.0 | 3.8 | 3.8 | 3.6 | 3.4 | 2.9 | 2.7 | 2.1 |
| 0.65 | -3.4 | -1.7 | -0.5 | 1.2 | 2.4 | 3.0 | 3.3 | 3.6 | 3.6 | 3.7 | 3.6 | 3.5 | 3.3 | 3.3 | 2.5 | 2.4 | 1.7 |
| 0.70 | -2.9 | -1.3 | -0.3 | 1.2 | 2.3 | 2.8 | 2.8 | 3.1 | 3.1 | 3.2 | 3.2 | 3.1 | 2.9 | 2.9 | 2.0 | 1.9 | 1.1 |
| 0.75 | -2.8 | -1.4 | -0.4 | 0.8 | 1.8 | 2.4 | 2.1 | 2.4 | 2.6 | 2.5 | 2.6 | 2.5 | 2.3 | 2.5 | 1.3 | 1.3 | 0.5 |
| 0.80 | -2.9 | -1.8 | -0.9 | 0.3 | 1.2 | 1.8 | 1.3 | 1.6 | 1.7 | 1.8 | 1.8 | 1.8 | 1.5 | 1.9 | 0.5 | 0.6 | 0.1 |
| 0.85 | -3.4 | -2.3 | -1.6 | -0.4 | 0.4 | 1.0 | 0.5 | 0.7 | 0.8 | 0.9 | 0.9 | 0.9 | 0.6 | 0.2 | -0.3 | 0.0 | 0.1 |
| 0.90 | -4.6 | -3.2 | -2.6 | -1.3 | -0.3 | 0.1 | -0.5 | -0.4 | -0.2 | -0.2 | -0.1 | -0.1 | -0.3 | -0.8 | -1.4 | -1.0 | -0.9 |
| 0.95 | -6.5 | -5.1 | -4.0 | -2.6 | -1.9 | -1.1 | -0.7 | -1.9 | -1.8 | -1.5 | -1.4 | -1.4 | -1.5 | -2.0 | -2.7 | -2.2 | -1.9 |
| 1.00 | -9.4 | -7.8 | -6.5 | -5.0 | -3.8 | -3.0 | -2.3 | -1.9 | -1.8 | -1.5 | -1.4 | -1.4 | -1.5 | -2.0 | -2.7 | -3.6 | -4.4 |

## TABLE B-2.

### APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.
### TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND VAN DER WAALS EQUATION.

| $P_r$ \ $T_r$ | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | -1.0 | -0.7 | -0.5 | -0.3 | -0.1 | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.4 | 0.4 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 0.10 | -1.9 | -1.5 | -1.1 | -0.5 | -0.1 | 0.1 | 0.3 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 | 1.0 | 1.1 | 1.1 | 1.1 |
| 0.15 | -3.1 | -2.3 | -1.7 | -0.7 | -0.1 | 0.3 | 0.6 | 0.8 | 1.0 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.6 | 1.6 | 1.6 |
| 0.20 | -4.1 | -3.0 | -2.1 | -0.8 | -0.0 | 0.5 | 0.9 | 1.3 | 1.4 | 1.7 | 1.8 | 1.9 | 2.1 | 2.1 | 2.2 | 2.2 | 2.1 |
| 0.25 | -5.4 | -3.7 | -2.7 | -0.9 | 0.2 | 0.9 | 1.3 | 1.6 | 2.0 | 2.2 | 2.3 | 2.5 | 2.6 | 2.7 | 2.7 | 2.8 | 2.7 |
| 0.30 | -6.7 | -4.7 | -3.7 | -0.9 | 0.4 | 1.1 | 1.8 | 2.2 | 2.4 | 2.7 | 2.9 | 3.1 | 3.1 | 3.3 | 3.4 | 3.4 | 3.3 |
| 0.35 | -7.9 | -5.6 | -4.3 | -1.0 | 0.5 | 1.6 | 2.2 | 2.7 | 3.0 | 3.2 | 3.5 | 3.6 | 3.7 | 3.9 | 3.9 | 3.8 | 3.8 |
| 0.40 | -8.8 | -6.2 | -4.4 | -1.1 | 0.7 | 1.9 | 2.7 | 3.1 | 3.5 | 3.8 | 3.9 | 4.1 | 4.3 | 4.4 | 4.4 | 4.4 | 4.3 |
| 0.45 | -10.2 | -6.7 | -4.6 | -1.2 | 0.9 | 2.3 | 3.1 | 3.6 | 4.0 | 4.3 | 4.5 | 4.7 | 4.8 | 4.9 | 4.9 | 4.9 | 4.7 |
| 0.50 | -10.5 | -7.0 | -4.4 | -1.0 | 1.0 | 2.6 | 3.4 | 4.1 | 4.3 | 4.7 | 4.9 | 5.1 | 5.3 | 5.3 | 5.3 | 5.2 | 4.9 |
| 0.55 | -9.9 | -7.1 | -4.3 | -0.5 | 1.2 | 2.8 | 3.7 | 4.5 | 4.9 | 5.2 | 5.4 | 5.6 | 5.8 | 5.8 | 5.8 | 5.6 | 5.2 |
| 0.60 | -9.2 | -6.5 | -3.9 | 0.0 | 1.7 | 3.2 | 4.2 | 4.9 | 5.4 | 5.6 | 5.8 | 6.1 | 6.2 | 6.2 | 6.2 | 5.9 | 5.5 |
| 0.65 | -9.5 | -5.8 | -3.1 | 0.6 | 2.2 | 3.8 | 4.7 | 5.5 | 5.9 | 6.3 | 6.4 | 6.6 | 6.7 | 6.6 | 6.5 | 6.2 | 5.7 |
| 0.70 | -8.3 | -4.9 | -2.1 | 1.0 | 2.8 | 4.3 | 5.2 | 5.9 | 6.3 | 6.7 | 6.8 | 7.0 | 7.1 | 7.0 | 6.8 | 6.4 | 5.9 |
| 0.75 | -7.5 | -4.2 | -1.1 | 1.7 | 3.7 | 4.6 | 5.6 | 6.3 | 6.7 | 7.0 | 7.3 | 7.3 | 7.5 | 7.4 | 7.1 | 6.5 | 5.9 |
| 0.80 | -6.5 | -3.4 | 0.0 | 2.4 | 4.0 | 5.1 | 5.9 | 6.6 | 7.1 | 7.3 | 7.5 | 7.7 | 7.7 | 7.6 | 7.2 | 6.7 | 6.0 |
| 0.85 | -5.3 | -2.3 | 1.8 | 3.3 | 5.4 | 5.5 | 6.3 | 6.9 | 7.3 | 7.5 | 7.8 | 8.0 | 8.0 | 7.8 | 7.4 | 6.9 | 6.2 |
| 0.90 | -4.0 | -1.0 | 2.5 | 4.2 | 5.8 | 6.5 | 6.9 | 7.4 | 7.7 | 8.0 | 8.1 | 8.2 | 8.2 | 8.0 | 7.5 | 6.9 | 6.2 |
| 0.95 | -2.1 | 0.0 | 2.7 | 4.4 | 5.8 | 6.6 | 7.2 | 7.7 | 8.0 | 8.4 | 8.4 | 8.5 | 8.4 | 8.1 | 7.6 | 6.9 | 6.1 |
| 1.00 | -1.1 | 0.9 | 2.8 | 4.3 | 5.4 | 6.3 | 7.5 | 7.9 | 8.1 | 8.4 | 8.5 | 8.6 | 8.5 | 8.2 | 7.6 | 6.8 | 6.1 |
| 1.05 | -0.0 | 1.5 | 2.3 | 4.1 | 4.3 | 6.6 | 7.4 | 7.4 | 8.1 | 8.0 | 8.2 | 8.3 | 8.4 | 8.1 | 7.5 |  |  |
| 1.10 | 0.7 | 1.6 | 1.2 | 3.7 | 4.0 | 6.3 | 7.2 | 6.8 | 7.7 | 7.4 | 7.7 | 7.8 | 8.1 | 7.9 |  |  |  |
| 1.15 | 3.5 | 1.6 | 0.2 | 2.9 | 4.0 | 5.5 | 6.9 | 5.5 | 7.2 | 6.6 | 7.0 | 7.2 | 7.6 |  |  |  |  |
| 1.20 | 7.9 | 0.5 | -2.2 | 1.9 | 3.0 | 4.8 | 5.2 | 5.0 | 6.3 | 5.8 | 6.3 | 6.6 | 7.1 |  |  |  |  |
| 1.25 | -13.8 | -1.1 | -5.1 | 0.1 | 1.7 | 4.0 | 5.4 | 4.0 | 5.5 | 4.8 | 5.2 | 5.6 |  |  |  |  |  |
| 1.30 | -20.9 | -4.6 | -9.1 | -1.3 | 0.1 | 2.7 | 4.6 |  | 4.4 |  |  |  |  |  |  |  |  |
| 1.35 | -27.9 | -8.4 | -12.8 | -1.7 | -1.6 | 1.2 | 3.4 |  |  |  |  |  |  |  |  |  |  |
| 1.40 | -37.4 | -13.2 | -16.8 | -3.0 |  |  | 2.2 |  |  |  |  |  |  |  |  |  |  |
| 1.45 |  | -18.1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 1.50 |  | -23.8 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

the $ZT_r$ isochores by the various two-parameter equations of state is given in Table B-3.

## B.3   Berthelot Equation

Berthelot's equation is simply a modified van der Waals equation in which the cohesive pressure term has been given a temperature dependence.

$$P + a/(TV^2) = RT/(V - b) \tag{B-15}$$

The two-parameters, a and b, are related to the critical temperature and critical pressure by the following equations.

$$a = 27 \ R^2 T_c^3/(64 \ P_c) \qquad b = RT_c/(8 \ P_c) \tag{B-16}$$

The reduced form of the equation is

$$P_r + 3/(V_r T_r) = 8 \ T_r/\{3(V_r - 1/3)\} \tag{B-17}$$

and $Z_c = 3/8$ the same as in van der Waals equation.  A density-implicit form for the compressibility factor is

$$Z = V_r/(V_r - 1/3) - 9/(8 \ T_r^2 V_r) \tag{B-18}$$

and the $ZT_r$ isochores are given by

$$ZT_r = V_r T_r/(V_r - 1/3) - 9/(8 \ T_r V_r) \tag{B-19}$$

When Equation B-19 is differentiated with respect to $T_r$ the isochores are shown to be curved with tangent slopes defined by

$$\left(\partial(ZT_r)/\partial T_r\right)_{V_r} = V_r/(V_r - 1/3) + 9/(8 \ T_r^2 V_r) \tag{B-20}$$

Equation B-19 predicts isochores which curve concave downward (i.e. $\partial^2(ZT_r)/\partial T_r^2 < 0$ ) for all reduced densities and temperatures.  Since the critical isochore is essentially

## TABLE B-3.

SUMMARY OF TWO-PARAMETER EQUATION OF STATE APPROXIMATIONS FOR THE $ZT_r$ ISOCHORES OF ROWLINSON'S CORRELATION

### Results Using Equation of State Critical Point Parameters

| Equation | $0.05 \leq \rho_r \leq 1.00$ | | | | $0.05 \leq \rho_r \leq 1.50$ | | | |
|---|---|---|---|---|---|---|---|---|
| | a | b | rms.% | max.% | a | b | rms.% | max.% |
| van der Waals | 1.1250 | 0.3333 | 6.41 | 28.1 | 1.1250 | 0.3333 | 7.81 | 43.3 |
| Berthelot | 1.1250 | 0.3333 | 14.78 | 34.5 | 1.1250 | 0.3333 | 19.78 | 49.1 |
| Dieterici | 2.0000 | 0.5000 | 15.94 | 32.6 | 2.0000 | 0.5000 | 20.45 | 41.9 |
| Redlich-Kwong | 1.2824 | 0.2599 | 3.71 | 13.9 | 1.2824 | 0.2599 | 4.60 | 18.9 |

### Results Using Least Squares Estimators

| Equation | $0.05 \leq \rho_r \leq 1.00$ | | | | $0.05 \leq \rho_r \leq 1.50$ | | | |
|---|---|---|---|---|---|---|---|---|
| | A | B | rms.% | max.% | A | B | rms.% | max.% |
| van der Waals | 1.4419 | 0.4327 | 2.51 | 9.4 | 1.2835 | 0.3670 | 5.49 | 37.4 |
| Berthelot | 1.0837 | 0.2083 | 4.51 | 38.7 | 0.9605 | 0.2197 | 9.43 | 76.8 |
| Dieterici | 1.8235 | 0.6007 | 5.15 | 33.0 | 1.7519 | 0.5415 | 8.29 | 76.5 |
| Redlich-Kwong | 1.4933 | 0.2996 | 1.14 | 4.8 | 1.4420 | 0.2840 | 1.92 | 7.9 |

linear, and the isochores for $V < V_c$ curve concave upward, it might be expected that Berthelot's equation would result in greater error at high density than van der Waals equation. This was indeed the case since Equation B-19 differed from the reduced correlation of Rowlinson by a standard error of 19.78 per cent compared to 7.81 per cent for van der Waals equation.

When the following modification of Equation B-17

$$ZT_r = T_r/(1 - B\rho_r) - A\rho_r/T_r \qquad (B-21)$$

was fitted to Rowlinson's correlation the standard errors were 4.51 per cent for $0.05 \leq \rho_r \leq 1.0$, and 9.43 per cent for $0.05 \leq \rho_r \leq 1.50$. Tables B-4 and B-5 show the percentage differences for these two density ranges. The least squares estimators for these density ranges and other pertinent data are summarized in Table B-3.

## B.4 Dieterici Equation

Dieterici proposed a two-parameter equation of state which contained an exponential term.

$$P = RT \exp(-a/RTV)/(V - b) \qquad (B-22)$$

The two constraints on the critical isotherm at the critical point may be used to evaluate the two parameters.

$$a = 4 R^2 T_c^2/(e^2 P_c) \qquad b = RT_c/(e^2 P_c) \qquad (B-23)$$

The reduced form of Dieterici's equation can be written as

$$P_r = e^2 T_r \exp(-2/V_r T_r)/\{2(V_r - 1/2)\} \qquad (B-24)$$

It should be noted that the equation predicts $Z_c = 2/e^2 \simeq$ 0.271 which is typical for a large number of substances.

## TABLE B-4.

### APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.
### TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND BERTHELOT EQUATION.

| $P_r$ \ $T_r$ | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | -1.2 | -1.1 | -1.1 | -1.1 | -1.0 | -1.0 | -0.9 | -0.8 | -0.7 | -0.6 | -0.6 | -0.6 | -0.4 | -0.4 | -0.2 | -0.2 | -0.1 |
| 0.10 | -2.3 | -2.3 | -2.2 | -2.1 | -2.0 | -1.8 | -1.7 | -1.5 | -1.5 | -1.4 | -1.2 | -1.1 | -0.8 | -0.7 | -0.5 | -0.3 | -0.2 |
| 0.15 | -3.5 | -3.4 | -3.4 | -3.1 | -2.9 | -2.7 | -2.5 | -2.4 | -2.1 | -1.9 | -1.7 | -1.5 | -1.2 | -1.0 | -0.7 | -0.5 | -0.3 |
| 0.20 | -4.6 | -4.5 | -4.3 | -4.0 | -3.7 | -3.5 | -3.2 | -2.9 | -2.3 | -2.4 | -2.2 | -1.9 | -1.4 | -1.1 | -0.8 | -0.5 | -0.3 |
| 0.25 | -5.9 | -5.6 | -5.4 | -4.9 | -4.5 | -4.1 | -3.9 | -3.6 | -3.2 | -2.8 | -2.6 | -2.2 | -1.8 | -1.2 | -0.9 | -0.5 | -0.2 |
| 0.30 | -7.1 | -6.7 | -6.3 | -5.7 | -5.2 | -4.8 | -4.4 | -4.0 | -3.7 | -3.2 | -2.9 | -2.5 | -1.9 | -1.3 | -0.8 | -0.4 | -0.1 |
| 0.35 | -8.0 | -7.8 | -7.4 | -6.5 | -5.9 | -5.3 | -4.9 | -4.4 | -3.9 | -3.6 | -3.1 | -2.3 | -2.0 | -1.2 | -0.7 | -0.3 | 0.1 |
| 0.40 | -8.6 | -8.5 | -8.3 | -7.3 | -6.5 | -5.9 | -5.2 | -4.8 | -4.3 | -3.8 | -3.3 | -2.8 | -2.0 | -1.2 | -0.6 | -0.1 | 0.3 |
| 0.45 | -8.7 | -8.9 | -8.7 | -8.0 | -7.0 | -6.2 | -5.6 | -5.0 | -4.5 | -4.0 | -3.4 | -2.8 | -1.9 | -1.1 | -0.5 | 0.1 | 0.5 |
| 0.50 | -8.5 | -9.0 | -9.0 | -8.4 | -7.6 | -6.7 | -6.1 | -5.3 | -4.9 | -4.1 | -3.5 | -2.9 | -1.8 | -1.0 | -0.2 | 0.3 | 0.7 |
| 0.55 | -7.7 | -8.6 | -8.8 | -8.7 | -8.0 | -7.0 | -6.3 | -5.4 | -4.7 | -3.9 | -3.4 | -2.7 | -1.6 | -0.7 | 0.0 | 0.7 | 1.0 |
| 0.60 | -5.7 | -7.3 | -8.1 | -8.5 | -7.9 | -7.1 | -6.3 | -5.1 | -4.6 | -3.5 | -3.2 | -2.5 | -1.3 | -0.3 | 0.5 | 1.0 | 1.4 |
| 0.65 | -3.0 | -5.6 | -7.1 | -7.9 | -7.6 | -6.8 | -6.0 | -4.8 | -4.3 | -3.7 | -2.9 | -2.1 | -0.8 | 0.0 | 0.9 | 1.5 | 1.8 |
| 0.70 | 0.2 | -3.3 | -5.5 | -7.1 | -7.0 | -6.4 | -5.7 | -4.4 | -4.0 | -2.2 | -2.5 | -1.7 | -0.3 | 0.5 | 1.4 | 1.9 | 2.2 |
| 0.75 | 4.0 | -0.8 | -3.7 | -6.2 | -6.5 | -6.1 | -5.3 | -3.8 | -3.6 | -2.2 | -1.9 | -1.2 | 0.1 | 1.2 | 2.0 | 2.4 | 2.7 |
| 0.80 | 8.7 | 2.2 | -1.5 | -4.8 | -5.6 | -5.3 | -4.8 | -3.1 | -2.9 | -1.0 | -1.3 | -0.5 | 0.8 | 1.9 | 2.6 | 3.1 | 3.4 |
| 0.85 | 14.5 | 6.2 | 1.3 | -3.1 | -4.3 | -4.3 | -3.9 | -1.9 | -2.3 | -0.3 | -0.6 | 0.2 | 1.5 | 2.6 | 3.4 | 3.9 | 4.2 |
| 0.90 | 21.4 | 11.0 | 4.7 | -0.7 | -2.5 | -2.9 | -2.5 | -0.7 | -1.2 | 0.5 | 0.3 | 1.1 | 2.4 | 3.5 | 4.2 | 4.8 | 5.0 |
| 0.95 | 29.4 | 16.3 | 9.0 | 1.9 | -0.8 | -1.4 | -1.2 | 0.7 | -0.1 | 1.9 | 1.4 | 2.2 | 3.5 | 4.4 | 5.1 | 5.6 | 5.8 |
| 1.00 | 38.7 | 22.4 | 13.3 | 4.4 | 1.1 | 0.1 | 0.2 | 0.6 | 1.1 | 1.9 | 2.6 | 3.4 | 4.6 | 5.6 | 6.2 | 6.5 | 6.8 |

# TABLE B-5.

APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.
TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND BERTHELOT EQUATION.

| Tr \ ρr | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | -1.9 | -1.8 | -1.7 | -1.6 | -1.5 | -1.3 | -1.3 | -1.1 | -1.0 | -0.9 | -0.8 | -0.8 | -0.6 | -0.5 | -0.3 | -0.3 | -0.2 |
| 0.10 | -3.8 | -3.6 | -3.5 | -3.2 | -2.9 | -2.6 | -2.4 | -2.2 | -2.0 | -1.7 | -1.7 | -1.5 | -1.2 | -1.0 | -0.8 | -0.6 | -0.4 |
| 0.15 | -5.9 | -5.6 | -5.4 | -4.8 | -4.3 | -3.9 | -3.6 | -3.3 | -3.0 | -2.9 | -2.4 | -2.2 | -1.8 | -1.5 | -1.1 | -0.9 | -0.6 |
| 0.20 | -8.0 | -7.6 | -7.1 | -6.3 | -5.6 | -5.2 | -4.7 | -4.2 | -4.1 | -3.5 | -3.1 | -2.8 | -2.2 | -1.8 | -1.4 | -1.1 | -0.8 |
| 0.25 | -10.5 | -9.6 | -9.0 | -7.9 | -7.0 | -6.3 | -5.8 | -5.2 | -4.7 | -4.2 | -4.1 | -3.4 | -2.8 | -2.1 | -1.7 | -1.2 | -0.8 |
| 0.30 | -13.0 | -11.9 | -10.9 | -9.4 | -8.3 | -7.5 | -6.7 | -6.0 | -5.6 | -4.8 | -3.8 | -3.9 | -3.4 | -2.3 | -1.8 | -1.2 | -0.8 |
| 0.35 | -15.4 | -14.2 | -13.1 | -11.0 | -9.7 | -8.5 | -7.7 | -6.9 | -6.1 | -5.0 | -4.3 | -4.3 | -3.6 | -2.4 | -1.9 | -1.3 | -0.7 |
| 0.40 | -17.7 | -15.3 | -15.2 | -12.7 | -10.9 | -9.6 | -8.5 | -7.6 | -6.8 | -5.4 | -4.8 | -4.7 | -3.8 | -2.6 | -1.8 | -1.1 | -0.7 |
| 0.45 | -19.5 | -18.5 | -16.8 | -14.3 | -12.2 | -10.5 | -9.3 | -8.2 | -7.5 | -5.7 | -5.1 | -4.9 | -3.8 | -2.7 | -1.9 | -1.1 | -0.6 |
| 0.50 | -21.5 | -20.0 | -18.6 | -15.8 | -13.2 | -11.6 | -10.2 | -9.0 | -8.0 | -6.4 | -6.1 | -5.2 | -3.7 | -2.7 | -1.8 | -1.1 | -0.5 |
| 0.55 | -21.0 | -21.4 | -19.7 | -16.1 | -14.7 | -11.6 | -11.0 | -9.9 | -8.3 | -6.9 | -6.3 | -5.3 | -3.5 | -2.5 | -1.8 | -1.0 | -0.4 |
| 0.60 | -23.4 | -22.4 | -20.6 | -17.9 | -15.4 | -12.9 | -11.8 | -10.1 | -8.5 | -7.3 | -6.4 | -5.4 | -3.2 | -2.2 | -1.3 | -0.8 | -0.1 |
| 0.65 | -23.5 | -22.4 | -21.3 | -18.9 | -16.0 | -13.0 | -12.0 | -10.2 | -8.7 | -7.2 | -6.3 | -5.1 | -2.8 | -1.4 | -0.7 | 0.0 | 0.0 |
| 0.70 | -25.3 | -20.7 | -21.4 | -19.3 | -16.2 | -13.9 | -12.1 | -10.1 | -8.1 | -7.2 | -6.2 | -4.8 | -2.4 | -1.0 | -0.3 | 0.3 | 0.3 |
| 0.75 | -22.8 | -18.1 | -21.4 | -18.8 | -16.6 | -14.2 | -12.1 | -9.8 | -7.3 | -6.4 | -5.9 | -4.4 | -1.9 | -0.3 | 0.1 | 0.8 | 0.7 |
| 0.80 | -21.8 | -16.5 | -20.7 | -17.6 | -16.5 | -13.0 | -11.3 | -9.0 | -7.2 | -5.7 | -5.6 | -3.8 | -1.2 | 0.3 | 0.7 | 1.3 | 1.3 |
| 0.85 | -20.0 | -13.6 | -17.9 | -16.2 | -14.5 | -11.1 | -10.3 | -8.2 | -6.0 | -5.0 | -4.1 | -3.2 | -0.2 | 1.1 | 1.4 | 1.5 | 1.9 |
| 0.90 | -20.0 | -10.3 | -15.0 | -14.3 | -13.3 | -10.0 | -9.1 | -7.2 | -5.4 | -3.6 | -3.2 | -2.3 | 0.6 | 2.1 | 2.1 | 2.2 | 2.6 |
| 0.95 | -17.5 | -6.5 | -12.0 | -13.3 | -11.2 | -9.1 | -8.1 | -6.3 | -4.7 | -2.0 | -1.7 | -1.3 | 1.6 | 3.1 | 3.1 | 2.9 | 3.3 |
| 1.00 | -14.0 | -1.8 | -9.9 | -12.0 | -10.0 | -8.1 | -7.3 | -5.4 | -3.9 | -1.3 | -0.7 | -0.4 | 2.7 | 4.2 | 4.1 | 3.7 | 4.2 |
| 1.05 | -9.5 | -6.0 | -7.4 | -9.4 | -9.4 | -6.8 | -6.4 | -4.5 | -2.9 | -0.4 | 0.1 | 0.5 | 3.8 | 5.4 | 5.2 | | |
| 1.10 | -4.3 | -11.0 | -4.5 | -7.4 | -7.6 | -6.6 | -5.1 | -3.6 | -2.0 | 0.0 | 1.0 | 1.4 | 4.8 | | | | |
| 1.15 | -1.5 | -6.5 | 2.9 | -4.5 | -5.5 | -4.7 | -3.5 | -2.1 | -0.6 | 0.8 | 2.3 | 2.4 | 6.1 | | | | |
| 1.20 | 8.4 | 11.8 | 6.4 | -1.8 | -3.2 | -2.9 | -1.8 | -0.5 | 0.6 | 2.1 | 3.5 | 3.7 | | | | | |
| 1.25 | 16.2 | 2.9 | 13.0 | 4.5 | 0.6 | 0.7 | 0.1 | | | | | 4.8 | | | | | |
| 1.30 | 24.3 | 6.4 | 4.5 | 9.6 | 3.2 | | | | | | | | | | | | |
| 1.35 | 33.2 | 13.5 | 11.8 | 14.2 | 0.6 | | | | | | | | | | | | |
| 1.40 | 43.0 | 19.8 | 1.3 | 9.9 | 2.3 | | | | | | | | | | | | |
| 1.45 | 53.8 | 26.4 | 4.8 | 19.9 | | | | | | | | | | | | | |
| 1.50 | 65.4 | 33.9 | 8.7 | 25.9 | | | | | | | | | | | | | |
| | 76.8 | 41.6 | 13.2 | | | | | | | | | | | | | | |

Dieterici's equation results in the following density-implicit form for the compressibility factor

$$Z = V_r \exp(-2/V_r T_r)/(V_r - 1/2) \qquad (B-25)$$

Thus, the $ZT_r$ isochores are given by the expression

$$ZT_r = V_r T_r \exp(-2/V_r T_r)/(V_r - 1/2) \qquad (B-26)$$

By differentiating Equation B-26 with respect to $T_r$ the tangent slopes of the $ZT_r$ isochores are obtained.

$$\left(\frac{\partial(ZT_r)}{\partial T_r}\right)_{V_r} = \left(\frac{V_r}{V_r - 1/2} + \frac{2}{(V_r - 1/2)T_r}\right)\exp(-2/V_r T_r) \qquad (B-27)$$

The second derivative of $ZT_r$ with respect to $T_r$

$$\left(\frac{\partial^2(ZT_r)}{\partial T_r^2}\right)_{V_r} = \left(\frac{4}{(V_r - 1/2)V_r T_r}\right)\exp(-2/V_r T_r) \qquad (B-28)$$

is positive for $V_r > 1/2$. Thus, Dieterici's equation predicts isochores which have curvature opposite to that of experimental evidence when $V_r > 1.0$.

When Equation B-26 was compared with Rowlinson's correlation for $1.0 \leq V_r \leq 20.0$ the standard error was 15.94 per cent. Equation B-26 may be written in terms of $\rho_r$

$$ZT_r = T_r \exp(-A\rho_r/T_r)/(1 - B\rho_r) \qquad (B-29)$$

and the parameters A and B evaluated using a least squares criterion. Tables B-6 and B-7 give the percentage errors for the least squares approximations. The equation gave a poor representation of the critical isotherm, and large errors occured along each isochore since the equation predicted the wrong curvature. Table B-3 summarizes the results and it is

## TABLE B-6.

### APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.
### TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND DIETERICI EQUATION.

| $Pr$ \\ $Tr$ | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.4 | 0.5 | 0.6 | 0.6 | 0.7 | 0.7 | 0.6 | 0.7 | 0.6 | 0.7 | 0.6 | 0.6 | 0.5 | 0.4 | 0.4 | 0.3 | 0.2 |
| 0.10 | 0.6 | 0.8 | 1.0 | 1.3 | 1.4 | 1.4 | 1.4 | 1.4 | 1.3 | 1.2 | 1.2 | 1.1 | 1.1 | 0.8 | 0.8 | 0.7 | 0.5 |
| 0.15 | 0.4 | 0.9 | 1.2 | 1.7 | 2.0 | 2.1 | 2.1 | 2.0 | 2.0 | 1.9 | 1.8 | 1.7 | 1.5 | 1.3 | 1.1 | 0.9 | 0.7 |
| 0.20 | 0.8 | 0.8 | 1.4 | 2.2 | 2.6 | 2.7 | 2.8 | 2.8 | 2.6 | 2.6 | 2.4 | 2.3 | 2.1 | 1.7 | 1.5 | 1.2 | 0.9 |
| 0.25 | -0.8 | -0.2 | 1.3 | 2.5 | 3.1 | 3.4 | 3.4 | 3.3 | 3.3 | 3.2 | 3.0 | 2.9 | 2.4 | 2.1 | 1.7 | 1.4 | 1.0 |
| 0.30 | -2.0 | -1.2 | 1.0 | 2.7 | 3.5 | 3.9 | 4.0 | 4.0 | 3.9 | 3.8 | 3.6 | 3.4 | 2.9 | 2.5 | 2.1 | 1.7 | 1.3 |
| 0.35 | -3.3 | -2.2 | 0.4 | 2.7 | 3.8 | 4.4 | 4.5 | 4.6 | 4.5 | 4.2 | 4.1 | 3.9 | 3.6 | 2.9 | 2.4 | 1.8 | 1.3 |
| 0.40 | -4.9 | -3.3 | -0.3 | 2.6 | 4.0 | 4.7 | 5.1 | 5.0 | 4.9 | 4.7 | 4.5 | 4.2 | 3.9 | 3.1 | 2.5 | 1.9 | 1.3 |
| 0.45 | -6.5 | -4.6 | -0.9 | 2.3 | 4.1 | 5.1 | 5.4 | 5.5 | 5.3 | 5.2 | 4.9 | 4.6 | 4.2 | 3.3 | 2.5 | 1.9 | 1.1 |
| 0.50 | -8.5 | -6.0 | -1.7 | 1.9 | 4.0 | 5.3 | 5.6 | 5.8 | 5.6 | 5.5 | 5.4 | 4.9 | 4.3 | 3.4 | 2.4 | 1.7 | 0.8 |
| 0.55 | -10.6 | -7.1 | -2.5 | 1.5 | 3.9 | 5.3 | 5.8 | 6.1 | 6.0 | 5.7 | 5.6 | 5.1 | 4.4 | 3.4 | 2.0 | 1.6 | 0.4 |
| 0.60 | -12.3 | -8.2 | -3.2 | 1.3 | 3.9 | 5.4 | 6.1 | 6.3 | 6.3 | 6.0 | 5.8 | 5.3 | 4.3 | 3.2 | 1.6 | 1.2 | 0.0 |
| 0.65 | -14.2 | -9.5 | -4.2 | 1.1 | 4.0 | 5.6 | 6.3 | 6.6 | 6.5 | 6.3 | 5.9 | 5.5 | 4.3 | 2.9 | 1.0 | 0.7 | -0.6 |
| 0.70 | -16.5 | -11.4 | -5.0 | 0.8 | 4.0 | 5.7 | 6.4 | 6.8 | 6.6 | 6.4 | 5.6 | 5.4 | 4.0 | 2.6 | 0.2 | -0.0 | -1.5 |
| 0.75 | -19.4 | -13.4 | -6.0 | 0.2 | 3.8 | 5.6 | 6.4 | 6.5 | 6.6 | 6.3 | 5.2 | 5.3 | 3.5 | 2.0 | -0.7 | -1.1 | -2.4 |
| 0.80 | -22.6 | -15.3 | -7.3 | -0.1 | 3.5 | 5.5 | 6.3 | 6.4 | 6.2 | 6.1 | 5.2 | 5.0 | 2.9 | 1.1 | -2.0 | -2.7 | -3.5 |
| 0.85 | -26.0 | -17.2 | -8.5 | -0.6 | 3.3 | 5.4 | 6.1 | 6.3 | 5.9 | 5.9 | 4.7 | 4.6 | 2.1 | 0.1 | -3.6 | -4.2 | -4.9 |
| 0.90 | -29.7 | -19.6 | -9.8 | -1.0 | 3.2 | 5.3 | 6.1 | 6.2 | 5.5 | 5.5 | 4.0 | 3.9 | 1.1 | -1.2 | -5.6 | -6.1 | -6.5 |
| 0.95 | -33.7 | -22.1 | -10.8 | -1.4 | 2.7 | 4.9 | 5.7 | 5.8 | 5.5 | 4.8 | 3.0 | 3.1 | -0.3 | -3.5 | | -8.4 | -3.6 |
| 1.00 | -38.0 | | -12.5 | -2.6 | 2.0 | 4.2 | 5.1 | 5.1 | 4.5 | 3.9 | | 2.0 | | -2.8 | | | -11.1 |

## TABLE B-7.

APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.
TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND DIETERICI EQUATION.

| $T_r$ / $\rho_r$ | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.3 | 0.4 | 0.6 | 0.6 | 0.7 | 0.7 | 0.7 | 0.8 | 0.7 | 0.8 | 0.7 | 0.7 | 0.7 | 0.6 | 0.6 | 0.4 | 0.4 |
| 0.10 | 0.5 | 0.8 | 1.0 | 1.3 | 1.5 | 1.5 | 1.6 | 1.6 | 1.5 | 1.5 | 1.5 | 1.4 | 1.3 | 1.2 | 1.1 | 1.0 | 0.9 |
| 0.15 | 0.3 | 0.8 | 1.2 | 1.8 | 2.1 | 2.3 | 2.4 | 2.3 | 2.3 | 2.3 | 2.2 | 2.2 | 2.0 | 1.8 | 1.7 | 1.5 | 1.3 |
| 0.20 | 0.8 | 0.8 | 1.5 | 2.4 | 2.9 | 3.1 | 3.1 | 3.2 | 3.1 | 3.1 | 3.0 | 2.9 | 2.8 | 2.5 | 2.2 | 2.0 | 1.7 |
| 0.25 | -0.8 | 0.5 | 1.4 | 2.8 | 3.5 | 3.8 | 3.9 | 3.9 | 3.9 | 3.9 | 3.8 | 3.7 | 3.3 | 3.1 | 2.7 | 2.5 | 2.2 |
| 0.30 | -1.9 | 0.0 | 1.2 | 3.0 | 4.1 | 4.5 | 4.7 | 4.6 | 4.7 | 4.7 | 4.5 | 4.4 | 4.0 | 3.8 | 3.4 | 3.0 | 2.7 |
| 0.35 | -3.2 | -1.0 | 0.7 | 3.2 | 4.5 | 5.2 | 5.4 | 5.6 | 5.5 | 5.4 | 5.3 | 5.2 | 4.7 | 4.4 | 3.9 | 3.3 | 3.1 |
| 0.40 | -4.6 | -1.8 | 0.1 | 3.3 | 4.9 | 5.7 | 6.2 | 6.2 | 6.3 | 6.2 | 6.0 | 5.8 | 5.3 | 4.9 | 4.4 | 3.4 | 3.3 |
| 0.45 | -6.1 | -2.7 | -0.2 | 3.2 | 5.2 | 6.3 | 6.8 | 7.0 | 6.9 | 6.9 | 6.7 | 6.5 | 6.0 | 5.4 | 4.8 | 4.3 | 3.5 |
| 0.50 | -7.9 | -3.8 | -0.8 | 3.1 | 5.4 | 6.8 | 7.3 | 7.6 | 7.5 | 7.5 | 7.3 | 7.1 | 6.6 | 5.9 | 5.2 | 4.5 | 3.7 |
| 0.55 | -9.7 | -4.9 | -1.3 | 3.0 | 5.6 | 7.2 | 7.8 | 8.2 | 8.3 | 8.1 | 7.9 | 7.8 | 7.1 | 6.3 | 5.6 | 4.8 | 3.8 |
| 0.60 | -11.0 | -5.6 | -1.6 | 3.1 | 6.0 | 7.6 | 8.4 | 8.9 | 9.0 | 8.8 | 8.6 | 8.4 | 7.6 | 6.8 | 6.0 | 4.9 | 3.9 |
| 0.65 | -12.5 | -6.4 | -2.2 | 3.3 | 6.4 | 8.3 | 9.1 | 9.6 | 9.7 | 9.6 | 9.2 | 9.0 | 8.2 | 7.2 | 6.2 | 5.1 | 3.8 |
| 0.70 | -14.3 | -7.2 | -2.5 | 3.5 | 7.0 | 8.8 | 9.7 | 10.2 | 10.3 | 10.2 | 9.8 | 9.5 | 8.6 | 7.5 | 6.4 | 5.0 | 3.6 |
| 0.75 | -16.5 | -8.4 | -2.9 | 3.5 | 7.3 | 9.2 | 10.3 | 10.8 | 10.8 | 10.7 | 10.4 | 10.4 | 9.0 | 7.8 | 6.5 | 5.0 | 3.4 |
| 0.80 | -18.9 | -9.7 | -3.6 | 3.7 | 7.6 | 9.8 | 10.8 | 11.3 | 11.5 | 11.2 | 10.9 | 10.8 | 9.3 | 8.0 | 6.5 | 4.9 | 3.2 |
| 0.85 | -21.4 | -10.7 | -3.9 | 4.0 | 8.2 | 10.4 | 11.4 | 12.0 | 11.9 | 11.7 | 11.3 | 11.1 | 9.5 | 8.0 | 6.4 | 4.7 | 2.9 |
| 0.90 | -23.9 | -11.6 | -4.2 | 4.5 | 8.9 | 11.1 | 12.2 | 12.6 | 12.5 | 12.2 | 11.7 | 11.4 | 9.7 | 9.0 | 6.2 | 4.4 | 2.4 |
| 0.95 | -26.5 | -12.7 | -4.2 | 5.1 | 9.4 | 11.8 | 12.8 | 13.1 | 13.0 | 12.6 | 12.1 | 11.5 | 9.8 | 7.9 | 5.9 | 4.4 | 1.6 |
| 1.00 | -29.0 | -13.8 | -4.5 | 5.1 | 9.9 | 12.2 | 13.3 | 13.6 | 13.3 | 13.0 | 12.3 | 11.4 | 9.7 | 7.7 | 5.4 | 3.8 | 0.8 |
| 1.05 | -31.9 | -15.1 | -5.3 | 5.0 | 10.2 | 12.5 | 13.6 | 13.8 | 13.4 | 13.0 | 12.2 | 10.9 | 9.4 | 7.2 | 4.7 | 3.0 | |
| 1.10 | -35.2 | -16.6 | -5.8 | 4.9 | 10.1 | 12.2 | 13.4 | 13.6 | 13.2 | 12.6 | 11.8 | 10.1 | 8.9 | 6.5 | 3.9 | | |
| 1.15 | -38.5 | -17.8 | -6.6 | 4.9 | 9.9 | 11.9 | 13.0 | 13.2 | 12.7 | 12.0 | 11.1 | 9.0 | 8.0 | 5.5 | | | |
| 1.20 | -42.3 | -19.7 | -7.4 | 4.6 | 9.7 | 11.4 | 12.5 | 12.3 | 11.8 | 11.8 | 10.0 | 7.5 | 6.6 | | | | |
| 1.25 | -47.3 | -21.6 | -8.3 | 4.2 | 9.3 | 10.3 | 11.9 | 11.5 | 10.8 | 9.7 | 8.7 | 5.3 | 4.9 | | | | |
| 1.30 | -53.2 | -24.8 | -10.0 | 3.2 | 8.4 | 8.9 | 10.7 | 10.1 | 9.1 | 7.9 | 6.5 | | | | | | |
| 1.35 | -59.4 | -27.7 | -11.8 | 1.8 | 7.2 | | 9.1 | | | | | | | | | | |
| 1.40 | -65.4 | -31.0 | -14.5 | 0.0 | 5.6 | | | | | | | | | | | | |
| 1.45 | -69.9 | -34.0 | -17.0 | -2.3 | | | | | | | | | | | | | |
| 1.50 | -76.5 | -38.0 | -20.3 | -5.3 | | | | | | | | | | | | | |

apparent that Dieterici's equation gave the poorest represen-
tation of the correlation.

## B.5  Redlich-Kwong Equation

The Redlich-Kwong equation represents a remarkable im-
provement over the van der Waals equation which it closely
resembles.

$$P + a/\{T^{0.5}(V^2 + Vb)\} = TR/(V - b) \tag{B-30}$$

The parameters a and b are evaluated by applying the con-
straints $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T = 0$ at the critical
point with the result

$$a = R^2 T_c^{2.5}/\{9(\sqrt[3]{2} - 1)P_c\} = cR^2 T_c^{2.5}/P_c \tag{B-31}$$

$$b = (\sqrt[3]{2} - 1)RT_c/(3P_c) = dRT_c/P_c \tag{B-32}$$

Substitution of Equations B-31 and B-32 into Equation B-30
leads to the reduced form of the Redlich-Kwong equation.

$$P_r = 3 T_r/(V_r - d) - 9 c/\{T_r^{0.5}(V_r^2 + 3 dV_r)\} \tag{B-33}$$

The critical compressibility factor is 1/3, a value which is
too large to be representative of most substances.

The density-implicit form for the compressibility factor
in terms of $V_r$ and $T_r$ can be written

$$Z = V_r/(V_r - 3 d) - 3 c/\{T_r^{1.5}(V_r + 3 d)\} \tag{B-34}$$

and the $ZT_r$ isochores are given by

$$ZT_r = V_r T_r/(V_r - 3 d) - 3 c/\{T_r^{0.5}(V_r + 3 d)\} \tag{B-35}$$

A comparison of Equation B-35 with the reduced correlation of
Rowlinson resulted in standard errors of 3.71 per cent and

4.60 per cent for the density ranges $0.05 \leq \rho_r \leq 1.0$ and $0.05 \leq \rho_r \leq 1.50$, respectively. This represents a significant improvement over van der Waals equation. The chief reason for the improvement is the last term in Equation B-35 which contains $T_r^{-0.5}$. This term provides for the curvature of the isochores. It may be recalled that van der Waals equation predicted linear isochores, and that in Berthelot's equation the curvature was the result of a term containing $T_r^{-1}$.

The tangent slopes of the isochores predicted by Equation B-35 can be calculated from

$$\left(\frac{\partial (ZT_r)}{\partial T_r}\right)_{V_r} = \frac{V_r}{V_r - 3\ d} - \frac{1.5\ c}{T_r^{1.5}(V_r + 3\ d)} \tag{B-36}$$

which when again differentiated with respect to $T_r$ gives

$$\left(\frac{\partial^2 (ZT_r)}{\partial T_r^2}\right)_{V_r} = - \frac{2.25\ c}{T_r^{2.5}(V_r + 3\ d)} \tag{B-37}$$

showing the isochores to be concave downward for all reduced volumes.

The constants in Equation B-35 were replaced with least squares estimators A an B, and the following equation

$$ZT_r = T_r/(1 - B\rho_r) - A\rho_r/\{T_r^{0.5}(1 + B\rho_r)\} \tag{B-38}$$

was fitted to Rowlinson's correlation. For reduced densities in the range $0.05 \leq \rho_r \leq 1.0$, the standard error was 1.14 per cent, and Table B-8 shows the maximum error of 4.8 per cent to occur at the critical point. When Equation B-38 was fitted to reduced densities in the range $0.05 \leq \rho_r \leq 0.7$, all errors were less than one per cent.

## TABLE B-8.

APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.

TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND REDLICH-KWONG EQUATION.

| $P_r$ \ $T_r$ | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 |
| 0.10 | 0.6 | 0.6 | 0.6 | 0.5 | 0.5 | 0.4 | 0.4 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 0.3 |
| 0.15 | 0.8 | 0.8 | 0.7 | 0.7 | 0.7 | 0.6 | 0.6 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 | 0.5 |
| 0.20 | 1.0 | 1.0 | 1.0 | 1.0 | 0.9 | 0.8 | 0.7 | 0.5 | 0.5 | 0.5 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| 0.25 | 0.8 | 1.0 | 1.0 | 1.1 | 1.0 | 0.9 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.8 | 0.7 |
| 0.30 | 0.6 | 0.8 | 1.0 | 1.0 | 1.1 | 1.0 | 0.8 | 0.8 | 0.7 | 0.7 | 0.7 | 0.7 | 0.8 | 1.0 | 0.9 | 1.0 | 1.0 |
| 0.35 | 0.4 | 0.5 | 0.6 | 0.7 | 0.9 | 0.8 | 0.8 | 0.7 | 0.7 | 0.7 | 0.6 | 0.7 | 0.8 | 1.0 | 1.0 | 1.2 | 1.1 |
| 0.40 | 0.3 | 0.4 | 0.3 | 0.3 | 0.8 | 0.7 | 0.8 | 0.6 | 0.5 | 0.6 | 0.6 | 0.6 | 0.8 | 1.0 | 1.1 | 1.3 | 1.1 |
| 0.45 | 0.4 | 0.2 | 0.2 | 0.0 | 0.6 | 0.3 | 0.2 | 0.4 | 0.2 | 0.1 | 0.4 | 0.5 | 0.8 | 1.0 | 1.1 | 1.3 | 1.2 |
| 0.50 | 0.4 | 0.0 | -0.1 | -0.4 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 0.1 | 0.3 | 0.5 | 0.8 | 1.0 | 1.3 | 1.3 | 1.2 |
| 0.55 | 0.5 | 0.0 | -0.1 | -0.6 | -0.3 | -0.4 | -0.3 | -0.2 | -0.2 | -0.1 | 0.2 | 0.4 | 0.8 | 1.1 | 1.3 | 1.2 | 1.1 |
| 0.60 | 1.3 | 0.3 | -0.1 | -0.9 | -0.6 | -0.7 | -0.5 | -0.5 | -0.0 | -0.0 | 0.1 | 0.3 | 0.9 | 1.2 | 1.4 | 1.2 | 1.1 |
| 0.65 | 2.1 | 0.6 | -0.1 | -1.1 | -1.2 | -1.0 | -0.8 | -0.8 | -0.2 | -0.0 | 0.1 | 0.3 | 0.9 | 1.3 | 1.4 | 1.3 | 1.1 |
| 0.70 | 2.8 | 1.0 | -0.4 | -1.7 | -1.7 | -1.6 | -1.7 | -1.2 | -0.5 | -0.2 | 0.1 | 0.3 | 0.9 | 1.3 | 1.4 | 1.3 | 1.0 |
| 0.75 | 3.2 | 0.9 | -0.8 | -2.1 | -2.3 | -2.0 | -2.0 | -1.5 | -0.7 | -0.4 | 0.0 | 0.3 | 0.9 | 1.3 | 1.4 | 1.2 | 1.1 |
| 0.80 | 3.6 | 0.8 | -1.0 | -2.5 | -2.6 | -2.3 | -2.2 | -1.5 | -1.0 | -0.5 | -0.0 | 0.3 | 0.9 | 1.3 | 1.4 | 1.3 | 1.2 |
| 0.85 | 4.0 | 0.9 | -1.0 | -2.7 | -2.8 | -2.5 | -2.0 | -1.5 | -1.0 | -0.5 | -0.1 | 0.3 | 0.9 | 1.4 | 1.6 | 1.5 | 1.3 |
| 0.90 | 4.4 | 0.9 | -1.2 | -2.9 | -3.2 | -2.9 | -2.2 | -1.5 | -1.0 | -0.5 | -0.1 | 0.3 | 0.9 | 1.4 | 1.6 | 1.6 | 1.4 |
| 0.95 | 4.7 | 0.6 | -1.2 | -3.0 | -3.2 | -3.2 | -2.2 | -1.6 | -1.0 | -0.5 | -0.0 | 0.4 | 1.1 | 1.5 | 1.6 | 1.6 | 1.4 |
| 1.00 | 4.8 | 0.3 | -1.8 | -3.6 | -3.7 | -3.2 | -2.4 | -1.7 | -1.2 | -0.5 | -0.0 | 0.5 | 1.3 | 1.7 | 1.8 | 1.7 | 1.6 |

For the 893 points with densities ranging from $0.05 \leq \rho_r \leq 1.50$, the standard error was 1.92 per cent. The percentage differences for a representative number of points are presented in Table B-9. It should be noted that the largest errors occur along the critical isotherm and the isochores for $\rho_r \geq 1.0$. A better fit for the critical isotherm would be obtained if $Z_c$ was a property which was entered into the equation such that the critical point was without error. The region for $\rho_r \geq 1.0$ is in error primarily because the equation predicts isochores which curve concave downward for all densities.

Table B-3 summarizes the results of approximating Rowlinson's correlation with the common two-parameter equations of state. The Redlich-Kwong equation was significantly better than the other equations tested. It is apparent, however, that all two-parameter equations have difficulty when the reduced density is greater than one.

## TABLE B-9.

APPROXIMATION OF ZT ISOCHORES FROM REDUCED CORRELATION BY ROWLINSON.
TABLE OF PERCENTAGE DIFFERENCES BETWEEN CORRELATION AND REDLICH-KWONG EQUATION.

| Pr \ Tr | 1.00 | 1.05 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 1.60 | 1.70 | 1.80 | 1.90 | 2.00 | 2.20 | 2.40 | 2.60 | 2.80 | 3.00 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.1 | 0.0 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 |
| 0.10 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 0.4 |
| 0.15 | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 | 0.5 | 0.5 | 0.5 | 0.6 |
| 0.20 | 0.3 | 0.4 | 0.5 | 0.6 | 0.6 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 | 0.6 | 0.6 | 0.7 | 0.7 | 0.7 | 0.7 | 0.8 |
| 0.25 | 0.0 | 0.3 | 0.4 | 0.6 | 0.7 | 0.7 | 0.5 | 0.7 | 0.6 | 0.7 | 0.7 | 0.7 | 0.7 | 0.9 | 0.8 | 1.0 | 1.0 |
| 0.30 | -0.3 | 0.0 | 0.3 | 0.6 | 0.8 | 0.8 | 0.7 | 0.9 | 0.7 | 0.8 | 0.8 | 0.9 | 0.9 | 1.1 | 1.1 | 1.2 | 1.3 |
| 0.35 | -0.6 | -0.3 | 0.0 | 0.5 | 0.6 | 0.8 | 0.8 | 0.7 | 0.9 | 0.8 | 0.9 | 1.0 | 1.1 | 1.3 | 1.3 | 1.4 | 1.5 |
| 0.40 | -0.8 | -0.5 | -0.4 | -0.1 | 0.5 | 0.6 | 0.6 | 0.6 | 0.8 | 0.8 | 0.9 | 1.0 | 1.3 | 1.4 | 1.5 | 1.6 | 1.6 |
| 0.45 | -0.9 | -0.7 | -0.5 | -0.4 | 0.3 | 0.6 | 0.3 | 0.4 | 0.7 | 0.9 | 0.9 | 1.1 | 1.4 | 1.5 | 1.6 | 1.8 | 1.8 |
| 0.50 | -0.3 | -0.6 | -0.8 | -0.7 | -0.5 | 0.3 | 0.1 | 0.3 | 0.6 | 0.8 | 0.9 | 1.1 | 1.5 | 1.6 | 1.7 | 1.9 | 1.9 |
| 0.55 | -0.0 | -0.9 | -0.9 | -1.0 | -0.4 | 0.0 | 0.0 | 0.0 | 0.6 | 0.8 | 0.9 | 1.2 | 1.6 | 1.7 | 1.9 | 2.1 | 1.9 |
| 0.60 | 0.9 | -1.1 | -0.6 | -0.7 | -0.7 | 0.0 | -0.0 | 0.0 | 0.5 | 0.7 | 1.0 | 1.3 | 1.8 | 1.8 | 2.1 | 2.3 | 2.1 |
| 0.65 | 1.7 | -1.0 | -0.5 | -0.4 | -0.8 | -0.2 | -0.2 | -0.1 | 0.4 | 0.7 | 1.1 | 1.4 | 1.9 | 2.0 | 2.2 | 2.3 | 2.2 |
| 0.70 | 2.3 | 0.0 | -0.6 | -1.0 | -1.2 | -0.5 | -0.4 | 0.0 | 0.5 | 0.8 | 1.2 | 1.5 | 2.1 | 2.2 | 2.4 | 2.4 | 2.3 |
| 0.75 | 3.0 | 1.1 | -0.6 | -1.1 | -1.4 | -0.8 | -0.7 | -0.1 | 0.8 | 0.9 | 1.2 | 1.6 | 2.2 | 2.4 | 2.6 | 2.5 | 2.6 |
| 0.80 | 3.8 | 1.6 | -0.4 | -1.1 | -1.5 | -1.0 | -0.4 | 0.2 | 0.9 | 1.3 | 1.5 | 1.8 | 2.4 | 2.6 | 2.8 | 2.8 | 2.9 |
| 0.85 | 4.7 | 2.3 | 0.2 | -1.0 | -1.7 | -0.9 | -0.6 | 0.0 | 1.0 | 1.6 | 2.1 | 2.3 | 2.6 | 2.8 | 3.0 | 3.1 | 3.1 |
| 0.90 | 5.7 | 3.0 | 0.8 | -0.4 | -2.1 | -1.4 | -0.9 | -0.2 | 0.9 | 1.7 | 2.3 | 2.6 | 3.0 | 3.1 | 3.3 | 3.3 | 3.4 |
| 0.95 | 6.7 | 3.9 | 1.2 | -0.6 | -2.6 | -1.9 | -1.0 | -0.3 | 0.8 | 1.5 | 2.4 | 2.9 | 3.4 | 3.4 | 3.6 | 3.6 | 3.7 |
| 1.00 | 7.4 | 4.6 | 1.8 | -1.1 | -2.8 | -2.1 | -1.2 | -0.2 | 1.0 | 1.6 | 2.4 | 3.1 | 3.8 | 3.9 | 4.0 | 3.9 | |
| 1.05 | 7.7 | 5.0 | 2.2 | -1.2 | -3.1 | -2.4 | -1.2 | -0.3 | 0.9 | 1.7 | 2.6 | 3.3 | 4.1 | 4.2 | 4.4 | | |
| 1.10 | 7.9 | 5.3 | 2.8 | -1.6 | -3.3 | -2.9 | -1.3 | 0.2 | 0.8 | 1.5 | 2.6 | 3.5 | 4.5 | 4.7 | 4.9 | | |
| 1.15 | 7.7 | 5.2 | 2.9 | -2.0 | -3.4 | -3.1 | -1.1 | 0.3 | 0.7 | 1.6 | 2.6 | 3.5 | 4.7 | 5.2 | | | |
| 1.20 | 7.0 | 0.7 | 1.8 | -3.0 | -3.8 | -3.3 | -1.2 | 0.3 | 0.7 | 1.5 | 2.7 | 3.6 | 5.0 | | | | |
| 1.25 | 6.4 | 1.4 | 1.2 | -3.3 | -3.1 | -2.2 | -1.1 | 0.2 | 0.6 | 1.7 | | | | | | | |
| 1.30 | 4.4 | 0.7 | 0.9 | -3.4 | -3.3 | -3.2 | -1.3 | | | | | | | | | | |
| 1.35 | 2.1 | -1.1 | -1.2 | -3.9 | -3.4 | -2.3 | | | | | | | | | | | |
| 1.40 | -0.1 | -2.4 | -2.9 | -4.6 | -3.2 | -2.4 | | | | | | | | | | | |
| 1.45 | -1.2 | -3.9 | -3.8 | -4.6 | | | | | | | | | | | | | |
| 1.50 | -3.2 | -4.6 | -5.0 | | | | | | | | | | | | | | |

APPENDIX C

COMPUTER PROGRAMS FOR CORRESPONDING STATES

DENSITY CORRELATIONS

```
      SUBROUTINE ZCOLL(DR,PR,TR,Z,ITER,IFLAG)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  A REDUCED 3-P-R EQUATION IS USED TO APPROXIMATE THE Z      *
C  FACTOR CORRELATION OF PILLITSON (TRANS. FARADAY SOCIETY,   *
C  VOL. 51, PP. 1317-1326, 1955).  IF IFLAG = 0, Z=Z(PR,TR)   *
C  IF IFLAG .GT. 0, Z=Z(DR,TR).                               *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION A(8)
      DATA A/0.36556695,0.99938220,0.55660621,0.35381582,
     1 0.44327453,0.10240614,0.53546923,0.54684921/
      ITER=0
      IF(TR-0.9)11,1,1
    1 IF(TR-4.5)2,2,11
    2 IF(IFLAG)3,3,10
    3 DR=1.0
      DO 8 ITER=1,10
      DR2=DR*DR
      T1=(A(1)*TR-A(2)-A(3)/TR**2)*DR
      T2=(A(4)*TR-A(5))*DR2
      T3=A(5)*A(6)*DR**5
      T4=A(7)*DR2/TR**2
      T5=A(8)*DR2
      T6=EXP(-T5)
      P=(TR+T1+T2+T3)*DR+T4*DR*(1.0+T5)*T6
      DP=TR+2.0*T1+3.0*T2+6.0*T3+T4*T6*(3.0+3.0*T5-2.0*T5*T5)
      DR1=DR-(P-0.293*PR)/DP
      IF(DR1)4,4,5
    4 DR1=0.5*DR
    5 IF(DR1-1.5)7,7,6
    6 DR1=DR+0.9*(1.5-DR)
    7 IF(ABS(DR-DR1)-0.00001)9,8,8
    8 DR=DR1
    9 Z=0.293*PR/(DR1*TR)
   10 DR2=DR*DR
      ITER=1
      Z=1.0+(A(1)-A(2)/TR-A(3)/TR**3)*DR+(A(4)-A(5)/TR)*DR2
     1 +A(5)*A(6)*DR**5/TR+A(7)*DR2/TR**3*(1.0+A(8)*DR2)*
     2 EXP(-A(8)*DR2)
   11 RETURN
      END
```

```
      SUBROUTINE ZKATZ(PR,TR,Z,ITER)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  A REDUCED B-W-R EQUATION IS USED TO APPROXIMATE THE Z       *
C  FACTOR CORRELATION OF STANDING-KATZ (TRANS. AIME, VOL.      *
C  146, PP. 140-149, 1942).   THE B-W-R COEFFICIENTS WERE      *
C  CALCULATED FROM THE TABULAR DATA IN 'HANDBOOK OF NATURAL    *
C  GAS ENGINEERING', MCGRAW-HILL, 1959, PP. 710-717.          *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION A(8)
      DATA A/0.31506237,1.0467099,0.57832729,0.53530771,
     1 0.61232032,0.10488813,0.68157001,0.63446549/
      ITER=0
      DR=1.0
      IF(TR-1.05)10,1,1
    1 IF(TR-3.0)2,2,10
    2 IF(PR-15.0)3,3,10
    3 DO 8 ITER=1,10
      DR2=DR*DR
      T1=(A(1)*TR-A(2)-A(3)/TR**2)*DR
      T2=(A(4)*TR-A(5))*DR2
      T3=A(5)*A(6)*DR**5
      T4=A(7)*DR2/TR**2
      T5=A(8)*DR2
      T6=EXP(-T5)
      P=(TR+T1+T2-T3)*DR+T4*DR*(1.0+T5)*T6
      DP=TR+2.0*T1+3.0*T2-6.0*T3+T4*T6*(3.0+3.0*T5-2.0*T5*T5)
      DR1=DR-(P-0.270*PR)/DP
      IF(DR1)4,4,5
    4 DR1=0.5*DR
    5 IF(DR1-2.2)7,7,6
    6 DR1=DR+0.5*(2.2-DR)
    7 IF(ABS(DR-DR1)-0.00001)9,8,8
    8 DR=DR1
    9 Z=0.270*PR/(DR1*TR)
   10 RETURN
      END
```

```
      SUBROUTINE COMPZ(ALPHA,ZC,TR,PR,Z,KODE)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE SOLVES THE DENSITY IMPLICIT FORMULATION, *
C  DR-F(ALPHA,ZC,PR,DR,TR) = 0, BY INTERVAL HALVING          *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C       KODE = 1 FOR A NORMAL EXIT FROM THIS SUBROUTINE      *
C       KODE = 2 IF TR OR PR ARE OUTSIDE THE CORRELATION     *
C       KODE = 3 IF PR IS WITHIN 0.001 OF PRS                *
C       KODE = 4 IF MORE THAN 15 ITERATIONS ARE REQUIRED     *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C       STATEMENT OF RIEDEL'S SATURATED LIQUID EQUATION
      DRSL(A,T)=1.0+0.85*(1.0-T)+(1.930+0.20*(A-7.0))*
     1 (1.0-T)**0.3333333
      KODE=1
      ITER=0
      IF(TR-0.3)17,1,1
    1 IF(TR-30.)2,2,17
    2 IF(PR-30.0)3,3,17
    3 IF(PR-1.0)4,4,9
    4 IF(TR-1.0)5,5,9
C       STATEMENT OF RIEDEL'S VAPOR PRESSURE EQUATION
    5 PRS=EXP(ALPHA*ALOG(TR)-0.0838*(ALPHA-3.75)*
     1 (36.0/TR-35.0-TR**6+42.0*ALOG(TR)))
      IF(ABS(PR-PRS)-0.001)6,6,7
    6 DR=DRSL(ALPHA,TR)
      KODE=3
      GO TO 16
    7 IF(PR-PRS)8,6,9
    8 D1=0.0
      F1=-PR*ZC/TR
      D2=1.0
      F2=1.0-PR/TR
      GO TO 10
    9 D1=0.0
      F1=-PR*ZC/TR
      D2=3.1+10.0*(0.3-ZC)
      F2=FDR(ALPHA,ZC,PR,D2,TR)
   10 DR=0.5*(D1+D2)
      F3=FDR(ALPHA,ZC,PR,DR,TR)
      IF(F3)11,16,12
   11 D1=DR
      F1=F3
      GO TO 13
   12 D2=DR
      F2=F3
   13 ITER=ITER+1
C       TEST FOR CONVERGENCE
      IF(ABS(D1-D2)/D1-0.001)16,14,14
   14 IF(ITER-15)10,10,15
   15 KODE=4
   16 Z=PR*ZC/(DR*TR)
      RETURN
   17 KODE=2
      RETURN
      END
```

```
      FUNCTION FDR(ALPHA,ZC,PR,DR,TR)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBPROGRAM RETURNS F(DR) = DR-F(ALPHA,ZC,PR,DR,TR)   *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      IF(DR-1.0)1,1,2
    1 TRS=1.0
      PRS=1.0-(5.-1./ZC)*(1.-DR)**4+(4.-1./ZC)*(1.-DR)**5
      PD=PR-PRS
      PZ=PD/(1.0+(ZC*ALPHA-1.0)*DR**(0.8+0.05*PD))
      GO TO 3
    2 TRS=TROOT(ALPHA,ZC,DR)
C       STATEMENT OF RIEDEL'S VAPOR PRESSURE EQUATION
      PRS=EXP(ALPHA*ALOG(TRS)-0.0838*(ALPHA-3.75)*
    1 (36.0/TRS-35.0-TRS**6+42.0*ALOG(TRS)))
      PD=PR-PRS
      BASE=1.0/(ALPHA*ZC)
      PZ=PD*BASE**(DR**((1.0+5.47736*(BASE-0.53811785))*
    1 (5.07301*SQRT(DR)-5.37068*DR+1.66199*DR**1.5000)+
    2 0.0427438*SQRT(PD)))
    3 FDR=DR-(DR*TRS/ZC+PZ)*ZC/TR
      RETURN
      END




      FUNCTION TROOT(ALPHA,ZC,DR)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBPROGRAM USES NEWTON-RAPHSON ITERATION TO SOLVE   *
C  RIEDEL'S SATURATED LIQUID EQUATION FOR TRS               *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      T1=0.98
C       RIEDEL'S SATURATED LIQUID EQUATION
    1 F=1.0+0.85*(1.0-T1)+(1.93+0.2*(ALPHA-7.0))*(1.0-T1)**
    1 0.3333333
C       TR DERIVATIVE OF RIEDEL'S SATURATED LIQUID EQUATION
      DF=-0.85-(0.6433334+0.06665667*(ALPHA-7.0))/(1.0-T1)**
    1 0.6666667
      T2=T1-(F-DR)/DF
      IF(T2-1.0)3,2,2
C       TEST FOR CONVERGENCE
    2 T2=T1+0.9*(1.0-T1)
    3 IF(ABS(T2-T1)-0.000001)5,4,4
    4 T1=T2
      GO TO 1
    5 TROOT=T2
      RETURN
      END
```

APPENDIX D

COMPUTER PROGRAM TO SIMULATE

THE DEPLETION PERFORMANCE OF A CONSTANT VOLUME RESERVOIR

This appendix gives a listing of the FORTRAN computer program used to simulate the depletion performance of a constant volume reservoir containing a retrograde fluid. The liquid phase is assumed to be immobile and the reservoir pressure is depleted by stepwise removal of some of the vapor phase. The program uses the following calculation procedure. The system pressure is decreased to the next specified lower pressure, and the system composition is flashed. The moles of vapor and liquid are calculated and the resulting phase compositions are used to determine the phase densities from corresponding states correlations. Knowledge of these densities permits calculation of the retrograde liquid saturation, and the moles of vapor which must be removed to restore the system to the initial volume. A new system composition is calculated and the process repeated. The same calculation procedure is used for both binary and ternary mixtures. Since flash calculations need not be trial and error for binary mixtures, the program performs some unnecessary calculations for these mixtures.

The main program reads the input data, calculates certain variables required for the support subroutines, and provides the format for the printout. Several examples of the printout from this program are reproduced in Appendix E. The comment cards at the start of the main program provide a listing of all the support subroutines that are required. Some of the required subroutines were presented in Appendices A and C. Comment cards are also used to describe the function of each subroutine.

```
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C   THIS PROGRAM SIMULATES THE DEPLETION PERFORMANCE OF A      *
C   CONSTANT VOLUME (1.0 CU. FT.) RESERVOIR.  THE FOLLOWING    *
C   SUPPORT SUBROUTINES ARE REQUIRED, XTRAP, ROWE, KCHAO,       *
C   PHIY, FGAM, FLASH, CPRES, CTEMP, PARTN, INVER, ZKATZ,       *
C   COMPZ, FDR, TROOT.                                          *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
        DIMENSION  C(3),  X(3),  Y(3),  Z(3),  WM(3),  PC(3),
      1 VC(3),  TC(3),  ZC(3),  AC(3),  AF(3),  COMP(3),
      2 DI(3), VI(3), FNU(3), PHI(3), GAM(3), PP(20), NAME(60)
        COMMON NCOMP, KATZ, T, P, V, WM, PC, TC, AF, DI, VI,
      1 X, Y, Z, PHI, FNU, GAM, C, VC
        IREAD=5
        IRITE=6
      1 FORMAT(60A1)
      2 FORMAT(2I2,5F8.1)
      3 FORMAT(10F8.3)
      4 FORMAT(1X,A4,1X,F7.3,F7.1,F7.4,F7.2,3F7.4,3F7.2)
      5 FORMAT('1'////25X,'TABLE'//1X,60A1/' DEPLETION OF A CO',
      1'NSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION')
      6 FORMAT('0',19(1H-),' PURE COMPONENT DATA ',20(1H-)/
      17X,'MOLE WT      PC        VC        TC',11X,'PITZER  RIEDEL'/
      2' COMP  LB/MOLE  PSIA    FT**3   DEG R     ZC     OMEGA'
      3,'    ALPHA'/' ----  -------  ------  -----  ------ ',
      4' ------  ------  ------'/)
      7 FORMAT(1X,A4,F9.3,F8.1,F7.3,F9.2,F7.3,2F8.3)
      8 FORMAT('0',13(1H-),' SIMULATED DEPLETION PERFORMANCE ',
      114(1H-)/6X,'SYSTEM  VAPOR  LIQUID   K     P, PK  LIQ   '
      2,'VAPOR  LIQUID'/' COMP   COMP   COMP    COMP  VALUE   '
      3' PSIA VOL / CF/LB   CF/LB'/' ----',5(7H ------),
      4' ----  ------  ------'/)
      9 FORMAT(1X,A4,4F7.3,F7.0,F6.2,F7.3,F8.4)
     10 FORMAT(1X,A4,4F7.3)
     11 FORMAT('1',////20X,'TABLE',8X,'(CONT.)'//1X,60A1)
     12 FORMAT('0MOLES',F6.3,2F7.3,7X,F7.0,/)
     13 FORMAT(' ZKATZ ITER =',I3)
     14 FORMAT(' COMPZ KODE =',I3)
     15 READ(IREAD,2)NCOMP,KATZ,T,P,DP,PEND,PK
        IF(NCOMP)16,50,16
     16 READ(IREAD,1)NAME
        READ(IREAD,3)Z
        READ(IREAD,3)PP
        READ(IREAD,4)(COMP(I),WM(I),PC(I),VC(I),TC(I),ZC(I),
      1AF(I),AC(I),6P,DI(I),VI(I),I=1,NCOMP)
        T=T+459.69
        ZT=0.0
        IP=0
        WRITE(IRITE,5)NAME
        WRITE(IRITE,6)
        WRITE(IRITE,7)(COMP(I),WM(I),PC(I),VC(I),TC(I),
      1ZC(I),AF(I),AC(I),I=1,NCOMP)
        WRITE(IRITE,8)
```

```
      LINE=20+NCOMP
      GO TO 18
   17 WRITE(IRITE,11)NAME
      WRITE(IRITE,8)
      LINE=9+NCOMP
   18 IP=IP+1
      P=PP(IP)
      CALL XTRAP(PK,IV)
      IF(IV)20,24,22
   20 DO 21 I=1,NCOMP
      X(I)=Z(I)
      Y(I)=0.0
      C(I)=1.0
   21 CONTINUE
      DV=0.0
      GO TO 28
   22 DO 23 I=1,NCOMP
      X(I)=0.0
      Y(I)=Z(I)
      C(I)=1.0
   23 CONTINUE
      DL=0.0
   24 PPCV=0.0
      PTCV=0.0
      WV=0.0
C        CALCULATE PSEUDOCRITICAL PROPERTIES FOR V PHASE
      DO 25 I=1,NCOMP
      PPCV=PPCV+Y(I)*PC(I)
      PTCV=PTCV+Y(I)*TC(I)
      WV=WV+Y(I)*WM(I)
   25 CONTINUE
C        CALCULATE VAPOR DENSITY VIA STANDING-KATZ CORRELATION
      PRV=P/PPCV
      TRV=T/PTCV
      CALL ZKATZ(PRV,TRV,ZV,ITER)
      IF(ITER)26,26,27
   26 WRITE(IRITE,13)ITER
   27 DV=ZV*10.73159*T/(WV*P)
      IF(ZT)35,35,36
   35 ZT=1.0/(DV*WV)
   36 IF(IV)28,28,31
   28 PPCL=0.0
      PTCL=0.0
      PZCL=0.0
      PVCL=0.0
      PACL=0.0
      WL=0.0
C        CALCULATE PSEUDOCRITICAL PROPERTIES FOR L PHASE
      DO 29 I=1,NCOMP
      PVCL=PVCL+X(I)*VC(I)
      PACL=PACL+X(I)*AC(I)
      PTCL=PTCL+X(I)*TC(I)
      PZCL=PZCL+X(I)*ZC(I)
      WL=WL+X(I)*WM(I)
```

```
   29 CONTINUE
      PPCL=PZCL*10.73159*PTCL/PVCL
C        CALCULATE LIQUID DENSITY VIA L-G-H CORRELATION
      PRL=P/PPCL
      TRL=T/PTCL
      CALL COMPZ (PACL,PZCL,TRL,PRL,ZL,KODE)
      IF(KODE-1)34,30,34
   34 WRITE(IRITE,14)KODE
   30 DL=ZL*10.73159*T/(WL*P)
      IF(ZT)37,37,31
   37 ZT=1.0/(DL*WL)
C        CALCULATE MOLES OF LIQUID (ZX)
   31 ZX=(1.0-V)*ZT
      PL=100.0*DL*WL*ZX
      ZY=(1.0-PL/100.0)/(DV*WV)
C        ADD MOLES OF L AND V TO GET TOTAL MOLES (ZT)
      ZT=ZX+ZY
      WRITE(IRITE,9)COMP(1),Z(1),Y(1),X(1),C(1),P,PL,DV,DL
      WRITE(IRITE,10)(COMP(I),Z(I),Y(I),X(I),C(I),I=2,NCOMP)
      WRITE(IRITE,12)ZT,ZY,ZX,PK
      LINE=LINE+NCOMP+3
C        CALCULATE NEW SYSTEM COMPOSITION
      DO 32 I=1,NCOMP
      Z(I)=(ZY*Y(I)+ZX*X(I))/ZT
   32 CONTINUE
      IF(ABS(P-PEND)-1.0)40,40,33
   33 IF(LINE-56)18,17,17
   40 CONTINUE
      GO TO 15
   50 CALL EXIT
      END
```

```fortran
      SUBROUTINE XTRAP(PK,IV)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE USES THE APPROXIMATING FORMULA GIVEN BY   *
C  GREEN, K.J., AND HACKMUTH, K.H., PROC. 41ST ANNUAL CONV.  *
C  OF N.P.G.A., PP. 11-19, (1963), TO EXTEND THE K-VALUES    *
C  FROM KCHOA INTO THE RANGE FROM 0.7*PK TO PK.              *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION SPACE(36), C(3), C1(4,3), C2(4), A(4,4),
     1 D(4,4), U(4,4), P1(4)
      COMMON NCOMP, KATZ, T, P, V, SPACE, C
      SIGN=1.0
      IF(3000.0-PK)20,20,21
   20 SIGN=-1.0
   21 IF(P-(SIGN*0.1+0.6)*PK)1,1,2
    1 CALL ROWE(PK,IV)
      RETURN
    2 PSAVE=P
      P=500.0
      CALL ROWE(PK,IV)
      IF(PSAVE-PK)4,3,3
    3 IV=1
      V=1.0
      GO TO 11
    4 P=SIGN*0.1*PK
      DO 5 I=1,3
      P=P+PK*0.2
      CALL ROWE(PK,IV)
      P1(I)=P
      DO 5 J=1,NCOMP
      C1(I,J)=C(J)
      C1(4,J)=1.0
    5 CONTINUE
      P1(4)=PK
      DO 10 J=1,NCOMP
      E=0.75
      IF(J-2)7,6,6
    6 E=0.250
    7 DO 8 I=1,4
      A(I,1)=(1.0-P1(I)/PK)**E
      A(I,2)=1.0/P1(I)
      A(I,3)=P1(I)
      A(I,4)=1.0
    8 CONTINUE
      CALL PARTN(4,A,D,U)
      CALL INVER(4,A,D,U)
      DO 9 I=1,4
      C2(I)=0.0
      DO 9 K=1,4
      C2(I)=C2(I)+D(I,K)*C1(K,J)
    9 CONTINUE
      C(J)=C2(1)*(1.0-PSAVE/PK)**E+C2(2)/PSAVE+C2(3)*PSAVE
     1 +C2(4)
   10 CONTINUE
      CALL FLASH(IV)
   11 P=PSAVE
      RETURN
      END
```

```
      SUBROUTINE ROWE(PK,IV)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE CALCULATES THE CONVERGENCE PRESSURE OF   *
C  THE SYSTEM ACCORDING TO THE DEFINITION BY ROWE, A.M.,    *
C  S.P.E.J. 7, PP. 54-60, (1967).                           *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION WM(3),  PC(3),  TC(3), AF(3),  DI(3), VI(3),
     1 X(3), Y(3)
      COMMON NCOMP, KATZ, T, P, V, WM, PC, TC, AF, DI, VI,
     1 X, Y
    1 FORMAT('0TIE LINE DOES NOT INTERSECT CRIT. TEMP. LOCUS'/)
      IF(NCOMP-2)2,2,3
    2 Z3=0.0
      Z13=0.0
      GO TO 4
    3 CALL CTEMP(Z13,1,3)
      Z31=1.0-Z13
      IF(T-TC(2))4,5,5
    4 CALL CTEMP(Z12,1,2)
      Z1=Z12
      SLOPE=(Z13-Z12)/(Z12-1.0)
      ZZ=1.0-Z12
      GO TO 6
    5 CALL CTEMP(Z23,2,3)
      SLOPE=-Z13/Z23
      ZZ=Z23
    6 CALL KCHAO(IV)
      IF(IV)11,7,11
    7 IF(NCOMP-2)10,10,8
    8 SLANT=(Y(1)-X(1))/(Y(2)-X(2))
      Z2=(X(1)-SLANT*X(2)-Z13)/(SLOPE-SLANT)
      Z1=Z13+SLOPE*Z2
      Z3=1.0-Z1-Z2
      IF(Z2-ZZ)10,9,9
    9 WRITE(6,1)
      Z1=Z12
      Z3=1.0-Z12
   10 CALL CPRES(Z1,Z3,PK)
   11 RETURN
      END
```

```
      SUBROUTINE KCHAO(IV)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE CALCULATES EQUILIBRIUM RATIOS USING THE   *
C  METHOD OF CHAO, K.C., AND SEADER J.D., A.I.CH.E.J., 7,    *
C  PP. 598-605, (1961).                                       *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION WM(3),  PC(3),  TC(3), AF(3),  DI(3), VI(3),
     1 X(3), Y(3), Z(3), PHI(3), FNU(3), GAM(3), C(3), VC(3),
     2 F(3)
      COMMON NCOMP, KATZ, T, P, V, WM, PC, TC, AF, DI, VI,
     1 X, Y, Z, PHI, FNU, GAM, C, VC
    1 FORMAT(' KCHAO ITER EQUAL 30')
      S1=0.0
      S2=0.0
      DO 2 I=1,NCOMP
      X(I)=TC(I)*VC(I)
      S1=S1+X(I)
    2 CONTINUE
      DO 5 I=1,NCOMP
      X(I)=X(I)*Z(I)/S1
      S2=S2+X(I)
    5 CONTINUE
      DO 6 I=1,NCOMP
      X(I)=X(I)/S2
    6 CONTINUE
      CALL FGAM(0)
      DO 7 I=1,NCOMP
      Y(I)=GAM(I)*FNU(I)*X(I)
    7 CONTINUE
      VOLD=0.1
      ITER=0
    8 ITER=ITER+1
      SUMX=0.0
      SUMY=0.0
      DO 9 I=1,NCOMP
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
    9 CONTINUE
      DO 10 I=1,NCOMP
      X(I)=X(I)/SUMX
      Y(I)=Y(I)/SUMY
   10 CONTINUE
      CALL FGAM(1)
      CALL PHIY
      DO 13 I=1,NCOMP
      FV=PHI(I)*Y(I)*P
      FL=GAM(I)*X(I)*FNU(I)
      F(I)=SQRT(FV*FL)
      Y(I)=F(I)/(PHI(I)*P)
      X(I)=F(I)/(GAM(I)*FNU(I))
      IF(X(I))11,11,12
   11 C(I)=0.0
```

```
      GO TO 13
12 C(I)=Y(I)/X(I)
13 CONTINUE
      IF(ITER-3)8,8,14
14 CONTINUE
      CALL FLASH(IV)
      IF(IV)19,15,19
15 IF(ABS(V-VOLD)-0.00001)19,19,16
16 VOLD=V
      ITER=ITER+1
      IF(ITER-30)10,10,18
18 WRITE(6,1)
19 RETURN
      END
```

```
      SUBROUTINE PHIY
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE CALCULATES THE VAPOR FUGACITY (PHI) AND   *
C  COMPRESSIBILITY FACTOR (Z) FROM THE REDLICK-KWONG EQUAT-  *
C  ION OF STATE. BY SETTING KATZ = 1, Z IS CALCULATED FROM   *
C  THE KATZ-STANDING CORRELATION INSTEAD OF REDLICK-KWONG.   *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION WM(3),  PC(3),  TC(3), AF(3),  DI(3), VI(3),
     1 X(3), Y(3), Z(3), PHI(3), ARK(3), BRK(3)
      COMMON NCOMP, KATZ, T, P, V, WM, PC, TC, AF, DI, VI,
     1 X, Y, Z, PHI
    1 FORMAT(' Z R-K ITER EQUAL 30')
    2 FORMAT(' Z KATZ ITER =',I3)
      AMIX=0.0
      BMIX=0.0
      DO 3 I=1,NCOMP
      TR=T/TC(I)
      ARK(I)=SQRT(0.42748028/(PC(I)*TR**2.5))
      BRK(I)=0.08664035/(PC(I)*TR)
      BMIX=BMIX+BRK(I)*Y(I)
      AMIX=AMIX+ARK(I)*Y(I)
    3 CONTINUE
      AOB=AMIX*AMIX/BMIX
      IF(KATZ)4,4,9
    4 CON1=2.0
      CON2=BMIX*P+0.001
      DO 8 ITER=1,30
      ZAS=(CON1+CON2)/2.0
      H=BMIX*P/ZAS
      ZZ=1.0/(1.0-H)-AOB*(H/(1.0+H))
      DEL=ZZ-ZAS
      IF(ABS(DEL)-0.0001)12,12,5
    5 IF(DEL)6,6,7
    6 CON1=ZAS
      GO TO 8
    7 CON2=ZAS
    8 CONTINUE
      WRITE(6,1)
      RETURN
    9 PPC=0.0
      PTC=0.0
      DO 10 I=1,NCOMP
      PPC=PPC+Y(I)*PC(I)
      PTC=PTC+Y(I)*TC(I)
   10 CONTINUE
      PR=P/PPC
      TR=T/PTC
      CALL ZKATZ(PR,TR,ZZ,ITER)
      IF(ITER)11,11,12
   11 WRITE(6,2)ITER
      GO TO 4
   12 DO 13 I=1,NCOMP
      PHI(I)=EXP((ZZ-1.0)*BRK(I)/BMIX-ALOG(ZZ-BMIX*P)-
     1 AOB*(2.0*ARK(I)/AMIX-BRK(I)/BMIX)*ALOG(1.0+BMIX*P/ZZ))
   13 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE FGAM(KASE)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE CALCULATES LIQUID FUGACITY COEFFICIENTS  *
C  (FNU) FROM A CORRESPONDING STATES CORRELATION, AND THE   *
C  ACTIVIVITY COEFFICIENTS IN THE LIQUID SOLUTION (GAM)     *
C  FROM HILDEBRAND'S EQUATION FOR A REGULAR SOLUTION.       *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION WM(3),  PC(3),  TC(3), AF(3),  DI(3), VI(3),
     1 X(3), Y(3), Z(3), PHI(3), FNU(3), GAM(3), A(15,2)
      COMMON NCOMP, KATZ, T, P, V, WM, PC, TC, AF, DI, VI,
     1 X, Y, Z, PHI, FNU, GAM
      DATA A/2.43840,-2.24550,-0.34084,0.00212,-0.00223,
     1 0.10486,-0.03691,0.0,0.0,0.0,0.0,0.0,0.0,0.0,
     25.75748,-3.01761,-4.9850,2.02299,0.0,0.08427,0.26567,
     3-0.31138,-0.02655,0.02883,-4.238930,8.65808,-1.22060,
     4-3.15224,-C.025/
      IF(KASE)6,1,6
    1 DO 5 I=1,NCOMP
      J=2
      CORR=1.0
      IF(WM(I)-17.0)3,4,4
    3 J=1
    4 TR=T/TC(I)
      PR=P/PC(I)
      FPO=A(1,J)+A(2,J)/TR+A(3,J)*TR+A(4,J)*TR**2+A(5,J)*TR**3
     1+(A(6,J)+A(7,J)*TR+A(8,J)*TR**2)*PR+(A(9,J)+A(10,J)*TR
     2)*PR**2-ALOG(PR)/2.3025851
      FPI=A(11,J)+A(12,J)*TR+A(13,J)/TR+A(14,J)*TR**3+
     1 A(15,J)*(PR-0.60)
      FNU(I)=P*EXP((FPO+AF(I)*FPI)*2.3025851)
    5 CONTINUE
    6 CON1=0.0
      CON2=0.0
      DO 7 I=1,NCOMP
      DELMX=X(I)*VI(I)
      CON1=CON1+DELMX
      CON2=CON2+DELMX*DI(I)
    7 CONTINUE
      DELMX=CON2/CON1
      RT=1.987*T/1.80
      DO 8 I=1,NCOMP
      GAM(I)=EXP(VI(I)*(DI(I)-DELMX)**2/RT)
    8 CONTINUE
      RETURN
      END
```

```fortran
      SUBROUTINE FLASH(KODE)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C THIS SUBROUTINE CHECKS IF THE SYSTEM IS IN THE TWO PHASE *
C REGION, THEN PERFORMS AN EQUILIBRIUM FLASH CALCULATION   *
C USING A NEWTON-RAPHSON PROCEDURE TO LOCATE V.            *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION WM(3),  PC(3),  TC(3), AF(3),  DI(3), VI(3),
     1 X(3), Y(3), Z(3), PHI(3), FNU(3), GAM(3), C(3)
      COMMON NCOMP, KATZ, T, P, V, WM, PC, TC, AF, DI, VI,
     1 X, Y, Z, PHI, FNU, GAM, C
    1 FORMAT(' FLASH ITER EQUAL 10')
C     CHECK IF SYSTEM CAN BE FLASHED
      BP=0.0
      DP=0.0
      DO 10 I=1,NCOMP
      BP=BP+C(I)*Z(I)
      DP=DP+Z(I)/C(I)
   10 CONTINUE
      IF(BP-1.0)12,11,11
   11 IF(DP-1.0)13,14,14
C     KODE = -1 SYSTEM IS A SINGLE PHASE LIQUID
   12 KODE=-1
      V=0.0
      RETURN
C     KODE = 1 SYSTEM IS A SINGLE PHASE VAPOR
   13 KODE=1
      V=1.0
      RETURN
   14 KODE=0
C     KODE = 0 SYSTEM IS IN TWO PHASE REGION
      V=0.7
      DO 20 ITER=1,10
      F=0.0
      DF=0.0
      DO 15 I=1,NCOMP
      R=(C(I)-1.0)/((C(I)-1.0)*V+1.0)
      F=F+R*Z(I)
      DF=DF-R*R*Z(I)
   15 CONTINUE
      V1=V-F/DF
      IF(V1)16,16,17
   16 V1=V*0.5
      GO TO 19
   17 IF(V1-1.0)19,18,18
   18 V1=(V+1.0)*0.5
   19 V=V1
      IF(ABS(F)-0.000001)21,20,20
   20 CONTINUE
      WRITE(6,1)
   21 DO 22 I=1,NCOMP
      X(I)=Z(I)/((C(I)-1.0)*V+1.0)
      Y(I)=C(I)*X(I)
   22 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE CTEMP(Z,IL,IH)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE DETERMINES THE COMPOSITION OF THE BINARY *
C  MIXTURE WHOSE CRITICAL TEMPERATURE EQUALS THE SYSTEM     *
C  TEMPERATURE VIA THE CORRELATION OF ETTER, D.O., AND KAY, *
C  W.B., J. CHEM. ENG. DATA, VOL. 6, PP. 409-414, (1961).   *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION WM(3), PC(3), TC(3)
      COMMON NCOMP, KATZ, T, P, V, WM, PC, TC
      Z=1.0
      DO 22 K=1,5
      DO 20 J=1,10
      Z=Z-0.1**K
      WL=Z*WM(IL)
      WH=(1.0-Z)*WM(IH)
      AMW=(WM(IL)*WL+WM(IH)*WH)/(WL+WH)
      IF(WM(IL)-17.0)10,11,11
   10 A=420.0
      B=WL/(WL+WH)
      B=0.447-0.537*B**1.86
      GO TO 18
   11 IF(WM(IL)-31.0)12,13,13
   12 A=565.0
      B=0.454-10.0**(2.0/Z**2.37)
      GO TO 18
   13 IF(WM(IL)-45.0)14,15,15
   14 A=677.0
      B=0.452-0.209*Z**1.85
      GO TO 18
   15 IF(WM(IL)-59.0)16,17,17
   16 A=769.0
      B=0.447-10.0**(0.842/Z**1.78)
      GO TO 18
   17 A=TC(IL)
      B=0.344-290.0/WM(IL)**2*Z**(15.0/WM(IL)**0.556)
   18 TCM=A*(AMW/WM(IL))**B
      IF(ABS(TCM-T)-0.1)23,23,19
   19 IF(TCM-T)20,23,21
   20 CONTINUE
   21 Z=Z+0.1**K
   22 CONTINUE
   23 RETURN
      END
```

```
      SUBROUTINE CPRES(Z1,Z3,PK)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE DETERMINES THE CRITICAL PRESSURE OF A     *
C  SPECIFIED BINARY OR TERNARY MIXTURE VIA THE CORRELATION   *
C  OF ETTER, D.O., AND KAY, W.B., J. CHEM. ENG. DATA, VOL.   *
C  6, PP. 409-414, (1961).                                   *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      DIMENSION WM(3), PC(3), W(3), Z(3), X(3), A(3), B(3),
     1 C(3)
      COMMON NCOMP, KATZ, T, P, V, WM, PC
      Z(1)=Z1
      Z(2)=1.0-Z1-Z3
      Z(3)=Z3
      PK=0.0
      S=0.0
      WAV=0.0
      DO 10 I=1,NCOMP
      PK=PK+Z(I)*PC(I)
      W(I)=Z(I)*WM(I)
      S=S+W(I)
   10 CONTINUE
      DO 19 I=1,NCOMP
      W(I)=W(I)/S
      WAV=WAV+W(I)*WM(I)
      X(I)=Z(I)
      IF(WM(I)-17.0)11,12,12
   11 A(I)=137.0
      B(I)=1.073
      C(I)=-3.07
      X(I)=W(I)
      GO TO 19
   12 IF(WM(I)-31.0)13,14,14
   13 A(I)=28.6
      B(I)=1.595
      C(I)=-4.0
      GO TO 19
   14 IF(WM(I)-45.0)15,16,16
   15 A(I)=13.6
      B(I)=1.225
      C(I)=-4.3
      GO TO 19
   16 IF(WM(I)-59.0)17,18,18
   17 A(I)=9.24
      B(I)=1.234
      C(I)=-3.5
      GO TO 19
   18 A(I)=9400.0/WM(I)**1.71
      B(I)=2.06/WM(I)**0.115
   19 CONTINUE
      IF(NCOMP-2)20,20,21
   20 PK=PC(1)+(A(1)*X(1)**B(1)+C(1))*(WAV-WM(1))
      RETURN
   21 PK=PK+A(1)*X(1)**B(1)*(WAV-WM(1))+A(2)*(Z(2)/(1.0-Z(1))
     1 )**B(2)*(1.0-Z(1))*((WAV-W(1)*WM(1))/(1.0-W(1))-WM(2))
      RETURN
      END
```

Critical Temperature Calculations by the Method of Etter and Kay

Etter and Kay[52] observed that a log-log plot of the critical temperatures of a series of binary mixtures of alkanes (all mixtures having a common component) versus the average molecular weight of the mixture resulted in a family of straight lines. These lines converged to a common point representing the critical temperature and molecular weight of the lightest component in the mixture. Thus, they were able to correlate critical temperatures to within about one per cent using equations having the form

$$T_C = A(M_{Av}/M_L)^B$$

where: $T_C$ is the critical temperature of the binary mixture, °R,

A is a constant and represents the critical temperature of the light component in the mixture,

$M_{Av}$ is the average molecular weight calculated on a weight basis,

$M_L$ is the molecular weight of the light component,

B is the slope of the straight line expressed as a simple function of the composition.

Critical Pressure Calculations by the Method of Etter and Kay

Etter and Kay also observed that a plot of the critical pressures of a series of binary mixtures of alkanes (all mixtures having a common component) versus average molecular weight of the mixture resulted in a family of straight lines. These lines converged to a common point representing the critical pressure and molecular weight of the lightest component in the mixture. Thus, they were able to correlate critical pressures to within about two per cent by equations having the

form

$$P_c = P_{cL} + C(M_{Av} - M_L)$$

where:   $P_c$   is the critical pressure of the binary mixture, psia,

$P_{cL}$   is the critical pressure of the light component in the mixture, psia,

C   is the slope of the straight line expressed as a simple function of the composition,

$M_{Av}$   is the average molecular weight, calculated on a weight basis for binaries containing methane, and on a mole basis for other systems,

$M_L$   is the molecular weight of the light component.

Etter and Kay showed that the following relationship could be used to extend the procedure for binaries to multicomponent mixtures

$$P_c = \Sigma\, x_i P_{ci} + \Sigma\, \phi_i$$

where:   $\Sigma\, x_i P_{ci}$ is the pseudocritical pressure of the mixture,

$\Sigma\, \phi_i$ is the excess critical pressure of every binary mixture with the light component in the system, excepting the binary made up of the lightest and heaviest components in the system.

APPENDIX E

COMPUTER PRINTOUT FOR

SIMULATION OF DEPLETION PERFORMANCE RUNS

## TABLE E-1

RUN NO. 5, METHANE AND N-BUTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

-------------------- PURE COMPONENT DATA --------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C4 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 0.195 | 6.770 |

-------------- SIMULATED DEPLETION PERFORMANCE --------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.816 | 0.816 | 0.000 | 1.000 | 2250. | 0.00 | 0.073 | 0.0000 |
| C4 | 0.184 | 0.184 | 0.000 | 1.000 | | | | |
| MOLES | 0.570 | 0.570 | 0.000 | | 1934. | | | |
| C1 | 0.815 | 0.815 | 0.000 | 1.000 | 2000. | 0.00 | 0.082 | 0.0000 |
| C4 | 0.183 | 0.183 | 0.000 | 1.000 | | | | |
| MOLES | 0.511 | 0.511 | 0.000 | | 1934. | | | |
| C1 | 0.815 | 0.839 | 0.580 | 1.445 | 1750. | 7.54 | 0.103 | 0.0475 |
| C4 | 0.183 | 0.160 | 0.419 | 0.352 | | | | |
| MOLES | 0.438 | 0.391 | 0.047 | | 1934. | | | |
| C1 | 0.812 | 0.869 | 0.477 | 1.822 | 1500. | 9.98 | 0.138 | 0.0407 |
| C4 | 0.187 | 0.130 | 0.522 | 0.249 | | | | |
| MOLES | 0.366 | 0.301 | 0.064 | | 1934. | | | |
| C1 | 0.800 | 0.878 | 0.396 | 2.217 | 1250. | 9.15 | 0.178 | 0.0373 |
| C4 | 0.199 | 0.121 | 0.603 | 0.201 | | | | |
| MOLES | 0.307 | 0.240 | 0.059 | | 1934. | | | |
| C1 | 0.783 | 0.877 | 0.317 | 2.767 | 1000. | 7.87 | 0.232 | 0.0348 |
| C4 | 0.216 | 0.122 | 0.682 | 0.173 | | | | |
| MOLES | 0.237 | 0.186 | 0.050 | | 1934. | | | |
| C1 | 0.758 | 0.872 | 0.253 | 3.442 | 800. | 6.88 | 0.298 | 0.0331 |
| C4 | 0.241 | 0.127 | 0.746 | 0.170 | | | | |
| MOLES | 0.189 | 0.145 | 0.043 | | 1934. | | | |

## TABLE E-1 (CONT.)

RUN NO. 5, METHANE AND N-BUTANE AT 100 F.

-------------- SIMULATED DEPLETION PERFORMANCE ---------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.729 | 0.858 | 0.188 | 4.554 | 600. | 5.81 | 0.401 | 0.0318 |
| C4 | 0.270 | 0.141 | 0.811 | 0.174 | | | | |
| MOLES | 0.143 | 0.106 | 0.036 | | 1934. | | | |
| C1 | 0.688 | 0.823 | 0.121 | 6.758 | 400. | 4.46 | 0.582 | 0.0305 |
| C4 | 0.311 | 0.176 | 0.878 | 0.201 | | | | |
| MOLES | 0.097 | 0.069 | 0.027 | | 1934. | | | |
| C1 | 0.624 | 0.706 | 0.053 | 13.303 | 200. | 2.01 | 0.988 | 0.0294 |
| C4 | 0.375 | 0.293 | 0.946 | 0.309 | | | | |
| MOLES | 0.047 | 0.034 | 0.012 | | 1934. | | | |
| C1 | 0.537 | 0.627 | 0.035 | 17.626 | 150. | 1.19 | 1.184 | 0.0292 |
| C4 | 0.462 | 0.372 | 0.964 | 0.386 | | | | |
| MOLES | 0.033 | 0.026 | 0.007 | | 1934. | | | |

ZKATZ ITER = 0

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.500 | 0.500 | 0.000 | 1.000 | 100. | 0.00 | 1.520 | 0.0000 |
| C4 | 0.499 | 0.499 | 0.000 | 1.000 | | | | |
| MOLES | 0.017 | 0.017 | 0.000 | | 1934. | | | |

TABLE E-2

RUN NO. 13, METHANE AND N-BUTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------ PURE COMPONENT DATA ------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|---|---|---|---|---|---|---|---|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C4 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 0.195 | 6.770 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|---|---|---|---|---|---|---|---|---|
| C1 | 0.849 | 0.849 | 0.000 | 1.000 | 2000. | 0.00 | 0.092 | 0.0000 |
| C4 | 0.151 | 0.151 | 0.000 | 1.000 | | | | |
| MOLES | 0.482 | 0.482 | 0.000 | | 1912. | | | |
| C1 | 0.848 | 0.848 | 0.000 | 1.000 | 1750. | 0.00 | 0.107 | 0.0000 |
| C4 | 0.150 | 0.150 | 0.000 | 1.000 | | | | |
| MOLES | 0.416 | 0.415 | 0.000 | | 1934. | | | |
| C1 | 0.848 | 0.869 | 0.477 | 1.822 | 1500. | 3.39 | 0.138 | 0.0407 |
| C4 | 0.150 | 0.130 | 0.522 | 0.249 | | | | |
| MOLES | 0.345 | 0.323 | 0.021 | | 1934. | | | |
| C1 | 0.844 | 0.878 | 0.396 | 2.217 | 1250. | 3.74 | 0.178 | 0.0373 |
| C4 | 0.155 | 0.121 | 0.603 | 0.201 | | | | |
| MOLES | 0.279 | 0.255 | 0.024 | | 1934. | | | |
| C1 | 0.836 | 0.877 | 0.317 | 2.767 | 1000. | 3.19 | 0.232 | 0.0348 |
| C4 | 0.163 | 0.122 | 0.682 | 0.178 | | | | |
| MOLES | 0.216 | 0.196 | 0.020 | | 1934. | | | |
| C1 | 0.824 | 0.872 | 0.253 | 3.442 | 800. | 2.62 | 0.298 | 0.0331 |
| C4 | 0.175 | 0.127 | 0.746 | 0.170 | | | | |
| MOLES | 0.168 | 0.152 | 0.016 | | 1934. | | | |
| C1 | 0.811 | 0.858 | 0.188 | 4.554 | 600. | 1.89 | 0.401 | 0.0318 |
| C4 | 0.188 | 0.141 | 0.811 | 0.174 | | | | |
| MOLES | 0.122 | 0.111 | 0.011 | | 1934. | | | |

TABLE E-2    (CONT.)

RUN NO. 13, METHANE AND N-BUTANE AT 100 F.

------------ SIMULATED DEPLETION PERFORMANCE ------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.793 | 0.823 | 0.121 | 6.758 | 400. | 0.83 | 0.582 | 0.0305 |
| C4 | 0.206 | 0.176 | 0.878 | 0.201 | | | | |
| | | | | | | | | |
| MOLES | 0.077 | 0.072 | 0.005 | | 1934. | | | |
| | | | | | | | | |
| C1 | 0.776 | 0.776 | 0.000 | 1.000 | 200. | 0.00 | 1.119 | 0.0000 |
| C4 | 0.223 | 0.223 | 0.000 | 1.000 | | | | |
| | | | | | | | | |
| MOLES | 0.035 | 0.035 | 0.000 | | 1934. | | | |

## TABLE E-3

RUN NO. 1, METHANE AND N-PENTANE AT 99.5 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

-------------------------- PURE COMPONENT DATA --------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

-------------------- SIMULATED DEPLETION PERFORMANCE --------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.881 | 0.881 | 0.000 | 1.000 | 2500. | 0.00 | 0.074 | 0.0000 |
| C5 | 0.119 | 0.119 | 0.000 | 1.000 | | | | |
| MOLES | 0.588 | 0.588 | 0.000 | | 2410. | | | |
| C1 | 0.880 | 0.905 | 0.694 | 1.303 | 2250. | 10.83 | 0.091 | 0.0470 |
| C5 | 0.118 | 0.094 | 0.305 | 0.308 | | | | |
| MOLES | 0.527 | 0.457 | 0.069 | | 2410. | | | |
| C1 | 0.878 | 0.927 | 0.587 | 1.576 | 2000. | 11.62 | 0.113 | 0.0389 |
| C5 | 0.121 | 0.072 | 0.412 | 0.176 | | | | |
| MOLES | 0.464 | 0.388 | 0.076 | | 2410. | | | |
| C1 | 0.871 | 0.941 | 0.514 | 1.830 | 1750. | 11.63 | 0.139 | 0.0354 |
| C5 | 0.128 | 0.058 | 0.485 | 0.121 | | | | |
| MOLES | 0.403 | 0.327 | 0.075 | | 2410. | | | |
| C1 | 0.860 | 0.946 | 0.447 | 2.114 | 1500. | 10.74 | 0.169 | 0.0331 |
| C5 | 0.139 | 0.053 | 0.552 | 0.097 | | | | |
| MOLES | 0.344 | 0.275 | 0.068 | | 2410. | | | |
| C1 | 0.846 | 0.949 | 0.379 | 2.499 | 1250. | 9.90 | 0.212 | 0.0312 |
| C5 | 0.153 | 0.050 | 0.620 | 0.081 | | | | |
| MOLES | 0.286 | 0.224 | 0.062 | | 2410. | | | |
| C1 | 0.825 | 0.951 | 0.310 | 3.069 | 1000. | 9.13 | 0.276 | 0.0296 |
| C5 | 0.174 | 0.048 | 0.689 | 0.070 | | | | |
| MOLES | 0.231 | 0.175 | 0.056 | | 2410. | | | |

## TABLE E-3 (CONT.)

RUN NO. 1, METHANE AND N-PENTANE AT 99.5 F.

---------------- SIMULATED DEPLETION PERFORMANCE ---------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|--------|--------|--------|--------|--------|--------|--------|--------|
| C1 | 0.795 | 0.951 | 0.252 | 3.775 | 800. | 8.52 | 0.355 | 0.0284 |
| C5 | 0.204 | 0.048 | 0.747 | 0.064 | | | | |
| MOLES | 0.188 | 0.137 | 0.051 | | 2410. | | | |
| C1 | 0.760 | 0.943 | 0.191 | 4.945 | 600. | 7.89 | 0.482 | 0.0274 |
| C5 | 0.239 | 0.051 | 0.808 | 0.064 | | | | |
| MOLES | 0.147 | 0.100 | 0.046 | | 2410. | | | |
| C1 | 0.707 | 0.938 | 0.128 | 7.279 | 400. | 7.22 | 0.722 | 0.0264 |
| C5 | 0.292 | 0.061 | 0.871 | 0.071 | | | | |
| MOLES | 0.107 | 0.065 | 0.042 | | 2410. | | | |
| C1 | 0.622 | 0.926 | 0.096 | 9.609 | 300. | 6.85 | 0.943 | 0.0260 |
| C5 | 0.377 | 0.073 | 0.903 | 0.081 | | | | |
| MOLES | 0.088 | 0.048 | 0.039 | | 2410. | | | |
| C1 | 0.556 | 0.901 | 0.063 | 14.262 | 200. | 6.39 | 1.341 | 0.0256 |
| C5 | 0.443 | 0.098 | 0.936 | 0.104 | | | | |
| MOLES | 0.068 | 0.032 | 0.036 | | 2410. | | | |
| C1 | 0.457 | 0.876 | 0.046 | 18.909 | 150. | 6.13 | 1.688 | 0.0254 |
| C5 | 0.542 | 0.123 | 0.953 | 0.129 | | | | |
| MOLES | 0.058 | 0.024 | 0.034 | | 2410. | | | |
| C1 | 0.387 | 0.825 | 0.029 | 28.188 | 100. | 5.76 | 2.264 | 0.0252 |
| C5 | 0.612 | 0.174 | 0.970 | 0.179 | | | | |
| MOLES | 0.048 | 0.016 | 0.032 | | 2410. | | | |
| C1 | 0.293 | 0.786 | 0.022 | 35.134 | 80. | 5.57 | 2.617 | 0.0251 |
| C5 | 0.706 | 0.213 | 0.977 | 0.217 | | | | |
| MOLES | 0.044 | 0.012 | 0.031 | | 2410. | | | |
| C1 | 0.245 | 0.722 | 0.015 | 46.686 | 60. | 5.32 | 3.096 | 0.0250 |
| C5 | 0.754 | 0.277 | 0.984 | 0.281 | | | | |
| MOLES | 0.039 | 0.009 | 0.029 | | 2410. | | | |

TABLE E-4

RUN NO. 2, METHANE AND N-PENTANE AT 99.7 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

---------------------------- PURE COMPONENT DATA ----------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|--------|------|------|-------|------|-------|-------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

---------------- SIMULATED DEPLETION PERFORMANCE ----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|-------|-------|-------|-------|-------|-------|-------|-------|
| C1 | 0.911 | 0.911 | 0.000 | 1.000 | 2500. | 0.00 | 0.084 | 0.0000 |
| C5 | 0.089 | 0.089 | 0.000 | 1.000 | | | | |
| MOLES | 0.561 | 0.561 | 0.000 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.910 | 0.910 | 0.000 | 1.000 | 2250. | 0.00 | 0.093 | 0.0000 |
| C5 | 0.088 | 0.088 | 0.000 | 1.000 | | | | |
| MOLES | 0.508 | 0.503 | 0.000 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.910 | 0.927 | 0.587 | 1.577 | 2000. | 3.66 | 0.113 | 0.0389 |
| C5 | 0.088 | 0.072 | 0.412 | 0.176 | | | | |
| MOLES | 0.446 | 0.422 | 0.024 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.908 | 0.940 | 0.513 | 1.831 | 1750. | 5.17 | 0.139 | 0.0354 |
| C5 | 0.091 | 0.059 | 0.486 | 0.121 | | | | |
| MOLES | 0.385 | 0.351 | 0.033 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.903 | 0.945 | 0.447 | 2.115 | 1500. | 5.09 | 0.169 | 0.0331 |
| C5 | 0.096 | 0.054 | 0.552 | 0.097 | | | | |
| MOLES | 0.325 | 0.292 | 0.032 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.895 | 0.949 | 0.379 | 2.500 | 1250. | 4.85 | 0.212 | 0.0312 |
| C5 | 0.104 | 0.050 | 0.620 | 0.081 | | | | |
| MOLES | 0.267 | 0.237 | 0.030 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.884 | 0.951 | 0.309 | 3.070 | 1000. | 4.54 | 0.276 | 0.0296 |
| C5 | 0.115 | 0.048 | 0.690 | 0.070 | | | | |
| MOLES | 0.211 | 0.183 | 0.028 | | 2409. | | | |

TABLE  E-4    (CONT.)

RUN NO. 2, METHANE AND N-PENTANE AT 99.7 F.

------------- SIMULATED DEPLETION PERFORMANCE -------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.866 | 0.951 | 0.251 | 3.776 | 800. | 4.23 | 0.355 | 0.0284 |
| C5 | 0.133 | 0.048 | 0.748 | 0.065 | | | | |
| MOLES | 0.169 | 0.143 | 0.025 | | 2409. | | | |
| C1 | 0.845 | 0.948 | 0.191 | 4.948 | 600. | 3.87 | 0.482 | 0.0274 |
| C5 | 0.154 | 0.051 | 0.808 | 0.064 | | | | |
| MOLES | 0.128 | 0.105 | 0.022 | | 2409. | | | |
| C1 | 0.812 | 0.937 | 0.128 | 7.283 | 400. | 3.42 | 0.721 | 0.0264 |
| C5 | 0.187 | 0.062 | 0.871 | 0.071 | | | | |
| MOLES | 0.088 | 0.068 | 0.019 | | 2409. | | | |
| C1 | 0.755 | 0.926 | 0.096 | 9.614 | 300. | 3.15 | 0.943 | 0.0260 |
| C5 | 0.244 | 0.073 | 0.903 | 0.081 | | | | |
| MOLES | 0.069 | 0.050 | 0.018 | | 2409. | | | |
| C1 | 0.707 | 0.901 | 0.063 | 14.270 | 200. | 2.79 | 1.341 | 0.0256 |
| C5 | 0.292 | 0.098 | 0.936 | 0.105 | | | | |
| MOLES | 0.049 | 0.033 | 0.015 | | 2409. | | | |
| C1 | 0.631 | 0.876 | 0.046 | 18.920 | 150. | 2.57 | 1.687 | 0.0254 |
| C5 | 0.368 | 0.123 | 0.953 | 0.129 | | | | |
| MOLES | 0.039 | 0.025 | 0.014 | | 2409. | | | |
| C1 | 0.571 | 0.824 | 0.029 | 28.204 | 100. | 2.24 | 2.262 | 0.0252 |
| C5 | 0.428 | 0.175 | 0.970 | 0.180 | | | | |
| MOLES | 0.029 | 0.016 | 0.012 | | 2409. | | | |
| C1 | 0.482 | 0.786 | 0.022 | 35.154 | 80. | 2.07 | 2.614 | 0.0251 |
| C5 | 0.517 | 0.213 | 0.977 | 0.218 | | | | |
| MOLES | 0.025 | 0.013 | 0.011 | | 2409. | | | |
| C1 | 0.429 | 0.721 | 0.015 | 46.712 | 60. | 1.84 | 3.091 | 0.0250 |
| C5 | 0.570 | 0.278 | 0.984 | 0.282 | | | | |
| MOLES | 0.020 | 0.010 | 0.010 | | 2409. | | | |

## TABLE E-5

RUN NO. 8, METHANE AND N-PENTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

---------------------- PURE COMPONENT DATA ----------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

--------------- SIMULATED DEPLETION PERFORMANCE ---------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.936 | 0.936 | 0.000 | 1.000 | 2500. | 0.00 | 0.094 | 0.0000 |
| C5 | 0.064 | 0.064 | 0.000 | 1.000 | | | | |
| MOLES | 0.540 | 0.540 | 0.000 | | 2409. | | | |
| C1 | 0.935 | 0.935 | 0.000 | 1.000 | 2250. | 0.00 | 0.104 | 0.0000 |
| C5 | 0.063 | 0.063 | 0.000 | 1.000 | | | | |
| MOLES | 0.488 | 0.488 | 0.000 | | 2409. | | | |
| C1 | 0.935 | 0.935 | 0.000 | 1.000 | 2000. | 0.00 | 0.117 | 0.0000 |
| C5 | 0.063 | 0.063 | 0.000 | 1.000 | | | | |
| MOLES | 0.432 | 0.432 | 0.000 | | 2409. | | | |
| C1 | 0.935 | 0.940 | 0.513 | 1.831 | 1750. | 0.74 | 0.139 | 0.0355 |
| C5 | 0.063 | 0.059 | 0.486 | 0.121 | | | | |
| MOLES | 0.372 | 0.367 | 0.004 | | 2409. | | | |
| C1 | 0.935 | 0.945 | 0.446 | 2.116 | 1500. | 1.22 | 0.169 | 0.0331 |
| C5 | 0.064 | 0.054 | 0.553 | 0.098 | | | | |
| MOLES | 0.312 | 0.304 | 0.007 | | 2409. | | | |
| C1 | 0.933 | 0.949 | 0.379 | 2.502 | 1250. | 1.39 | 0.212 | 0.0312 |
| C5 | 0.066 | 0.050 | 0.620 | 0.081 | | | | |
| MOLES | 0.254 | 0.245 | 0.008 | | 2409. | | | |
| C1 | 0.929 | 0.951 | 0.309 | 3.072 | 1000. | 1.39 | 0.276 | 0.0296 |
| C5 | 0.070 | 0.048 | 0.690 | 0.070 | | | | |
| MOLES | 0.198 | 0.189 | 0.008 | | 2409. | | | |

TABLE E-5    (CONT.)

RUN NO. 8, METHANE AND N-PENTANE AT 100 F.

---------------- SIMULATED DEPLETION PERFORMANCE ----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.923 | 0.951 | 0.251 | 3.779 | 800. | 1.29 | 0.355 | 0.0284 |
| C5 | 0.076 | 0.048 | 0.748 | 0.065 | | | | |
| MOLES | 0.155 | 0.147 | 0.007 | | 2409. | | | |
| C1 | 0.915 | 0.947 | 0.191 | 4.951 | 600. | 1.10 | 0.482 | 0.0274 |
| C5 | 0.084 | 0.052 | 0.808 | 0.064 | | | | |
| MOLES | 0.114 | 0.108 | 0.006 | | 2409. | | | |
| C1 | 0.904 | 0.937 | 0.128 | 7.288 | 400. | 0.80 | 0.721 | 0.0264 |
| C5 | 0.095 | 0.062 | 0.871 | 0.071 | | | | |
| MOLES | 0.075 | 0.070 | 0.004 | | 2409. | | | |
| C1 | 0.886 | 0.900 | 0.063 | 14.282 | 200. | 0.22 | 1.340 | 0.0256 |
| C5 | 0.113 | 0.099 | 0.936 | 0.105 | | | | |
| MOLES | 0.035 | 0.034 | 0.001 | | 2409. | | | |
| C1 | 0.871 | 0.875 | 0.046 | 18.936 | 150. | 0.02 | 1.685 | 0.0254 |
| C5 | 0.128 | 0.124 | 0.953 | 0.130 | | | | |
| MOLES | 0.025 | 0.025 | 0.000 | | 2409. | | | |
| C1 | 0.870 | 0.870 | 0.000 | 1.000 | 100. | 0.00 | 2.521 | 0.0000 |
| C5 | 0.129 | 0.129 | 0.000 | 1.000 | | | | |
| MOLES | 0.016 | 0.016 | 0.000 | | 2409. | | | |
| C1 | 0.870 | 0.870 | 0.000 | 1.000 | 80. | 0.00 | 3.164 | 0.0000 |
| C5 | 0.129 | 0.129 | 0.000 | 1.000 | | | | |
| MOLES | 0.013 | 0.013 | 0.000 | | 2409. | | | |
| C1 | 0.870 | 0.870 | 0.000 | 1.000 | 60. | 0.00 | 4.237 | 0.0000 |
| C5 | 0.129 | 0.129 | 0.000 | 1.000 | | | | |
| MOLES | 0.010 | 0.010 | 0.000 | | 2409. | | | |
| C1 | 0.870 | 0.870 | 0.000 | 1.000 | 40. | 0.00 | 6.382 | 0.0000 |
| C5 | 0.129 | 0.129 | 0.000 | 1.000 | | | | |
| MOLES | 0.006 | 0.006 | 0.000 | | 2409. | | | |

## TABLE E-6

RUN NO. 9, METHANE AND N-PENTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------- PURE COMPONENT DATA -------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|--------|--------|--------|--------|--------|--------|--------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

-------------- SIMULATED DEPLETION PERFORMANCE --------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|--------|--------|--------|--------|--------|--------|--------|--------|
| C1 | 0.878 | 0.878 | 0.000 | 1.000 | 2500. | 0.00 | 0.074 | 0.0000 |
| C5 | 0.122 | 0.122 | 0.000 | 1.000 | | | | |
| MOLES | 0.590 | 0.590 | 0.000 | | 2409. | | | |
| C1 | 0.877 | 0.905 | 0.694 | 1.303 | 2250. | 12.03 | 0.091 | 0.0470 |
| C5 | 0.121 | 0.094 | 0.305 | 0.309 | | | | |
| MOLES | 0.528 | 0.451 | 0.077 | | 2409. | | | |
| C1 | 0.874 | 0.926 | 0.587 | 1.577 | 2000. | 12.35 | 0.113 | 0.0389 |
| C5 | 0.125 | 0.073 | 0.412 | 0.177 | | | | |
| MOLES | 0.465 | 0.384 | 0.081 | | 2409. | | | |
| C1 | 0.867 | 0.940 | 0.513 | 1.831 | 1750. | 12.24 | 0.139 | 0.0355 |
| C5 | 0.132 | 0.059 | 0.486 | 0.121 | | | | |
| MOLES | 0.404 | 0.324 | 0.079 | | 2409. | | | |
| C1 | 0.856 | 0.945 | 0.446 | 2.116 | 1500. | 11.26 | 0.169 | 0.0331 |
| C5 | 0.143 | 0.054 | 0.553 | 0.098 | | | | |
| MOLES | 0.345 | 0.273 | 0.072 | | 2409. | | | |
| C1 | 0.841 | 0.949 | 0.379 | 2.502 | 1250. | 10.37 | 0.212 | 0.0312 |
| C5 | 0.158 | 0.050 | 0.620 | 0.081 | | | | |
| MOLES | 0.288 | 0.223 | 0.065 | | 2409. | | | |
| C1 | 0.820 | 0.951 | 0.309 | 3.072 | 1000. | 9.55 | 0.276 | 0.0296 |
| C5 | 0.179 | 0.048 | 0.690 | 0.070 | | | | |
| MOLES | 0.232 | 0.174 | 0.058 | | 2409. | | | |

## TABLE E-6 (CONT.)

RUN NO. 9, METHANE AND N-PENTANE AT 100 F.

---------------- SIMULATED DEPLETION PERFORMANCE ----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.789 | 0.951 | 0.251 | 3.779 | 800. | 8.91 | 0.355 | 0.0284 |
| C5 | 0.210 | 0.048 | 0.748 | 0.065 | | | | |
| | | | | | | | | |
| MOLES | 0.190 | 0.136 | 0.053 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.752 | 0.947 | 0.191 | 4.951 | 600. | 8.27 | 0.482 | 0.0274 |
| C5 | 0.247 | 0.052 | 0.808 | 0.064 | | | | |
| | | | | | | | | |
| MOLES | 0.149 | 0.100 | 0.049 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.699 | 0.937 | 0.128 | 7.288 | 400. | 7.56 | 0.721 | 0.0264 |
| C5 | 0.300 | 0.062 | 0.871 | 0.071 | | | | |
| | | | | | | | | |
| MOLES | 0.109 | 0.065 | 0.044 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.612 | 0.900 | 0.063 | 14.282 | 200. | 6.62 | 1.340 | 0.0256 |
| C5 | 0.387 | 0.099 | 0.936 | 0.105 | | | | |
| | | | | | | | | |
| MOLES | 0.069 | 0.032 | 0.037 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.449 | 0.875 | 0.046 | 18.936 | 150. | 6.35 | 1.685 | 0.0254 |
| C5 | 0.550 | 0.124 | 0.953 | 0.130 | | | | |
| | | | | | | | | |
| MOLES | 0.060 | 0.024 | 0.035 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.379 | 0.823 | 0.029 | 28.228 | 100. | 5.97 | 2.259 | 0.0252 |
| C5 | 0.620 | 0.176 | 0.970 | 0.181 | | | | |
| | | | | | | | | |
| MOLES | 0.049 | 0.016 | 0.033 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.286 | 0.785 | 0.022 | 35.184 | 80. | 5.78 | 2.609 | 0.0251 |
| C5 | 0.713 | 0.214 | 0.977 | 0.219 | | | | |
| | | | | | | | | |
| MOLES | 0.045 | 0.012 | 0.032 | | 2409. | | | |
| | | | | | | | | |
| C1 | 0.238 | 0.720 | 0.015 | 46.751 | 60. | 5.52 | 3.085 | 0.0250 |
| C5 | 0.761 | 0.279 | 0.984 | 0.284 | | | | |
| | | | | | | | | |
| MOLES | 0.040 | 0.009 | 0.030 | | 2409. | | | |

TABLE E-7

RUN NO. 10, UHP METHANE AND N-PENTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------- PURE COMPONENT DATA -------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

--------------- SIMULATED DEPLETION PERFORMANCE ---------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.925 | 0.925 | 0.000 | 1.000 | 2500. | 0.00 | 0.089 | 0.0000 |
| C5 | 0.075 | 0.075 | 0.000 | 1.000 | | | | |
| MOLES | 0.549 | 0.549 | 0.000 | | 2409. | | | |
| C1 | 0.924 | 0.924 | 0.000 | 1.000 | 2250. | 0.00 | 0.099 | 0.0000 |
| C5 | 0.074 | 0.074 | 0.000 | 1.000 | | | | |
| MOLES | 0.496 | 0.496 | 0.000 | | 2409. | | | |
| C1 | 0.924 | 0.926 | 0.587 | 1.577 | 2000. | 0.40 | 0.113 | 0.0389 |
| C5 | 0.074 | 0.073 | 0.412 | 0.177 | | | | |
| MOLES | 0.439 | 0.436 | 0.002 | | 2409. | | | |
| C1 | 0.924 | 0.940 | 0.513 | 1.831 | 1750. | 2.53 | 0.139 | 0.0355 |
| C5 | 0.075 | 0.059 | 0.486 | 0.121 | | | | |
| MOLES | 0.377 | 0.360 | 0.016 | | 2409. | | | |
| C1 | 0.922 | 0.945 | 0.446 | 2.116 | 1500. | 2.78 | 0.169 | 0.0331 |
| C5 | 0.077 | 0.054 | 0.553 | 0.098 | | | | |
| MOLES | 0.317 | 0.299 | 0.017 | | 2409. | | | |
| C1 | 0.917 | 0.949 | 0.379 | 2.502 | 1250. | 2.79 | 0.212 | 0.0312 |
| C5 | 0.082 | 0.050 | 0.620 | 0.081 | | | | |
| MOLES | 0.259 | 0.241 | 0.017 | | 2409. | | | |
| C1 | 0.910 | 0.951 | 0.309 | 3.072 | 1000. | 2.66 | 0.276 | 0.0296 |
| C5 | 0.089 | 0.048 | 0.690 | 0.070 | | | | |
| MOLES | 0.203 | 0.187 | 0.016 | | 2409. | | | |

# TABLE E-7 (CONT.)

RUN NO. 10, UHP METHANE AND N-PENTANE AT 100 F.

-------------- SIMULATED DEPLETION PERFORMANCE --------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.899 | 0.951 | 0.251 | 3.779 | 800. | 2.48 | 0.355 | 0.0284 |
| C5 | 0.100 | 0.048 | 0.748 | 0.065 | | | | |
| MOLES | 0.161 | 0.146 | 0.015 | | 2409. | | | |
| C1 | 0.885 | 0.947 | 0.191 | 4.951 | 600. | 2.22 | 0.482 | 0.0274 |
| C5 | 0.114 | 0.052 | 0.808 | 0.064 | | | | |
| MOLES | 0.120 | 0.106 | 0.013 | | 2409. | | | |
| C1 | 0.864 | 0.937 | 0.128 | 7.288 | 400. | 1.86 | 0.721 | 0.0264 |
| C5 | 0.135 | 0.062 | 0.871 | 0.071 | | | | |
| MOLES | 0.080 | 0.069 | 0.010 | | 2409. | | | |
| C1 | 0.828 | 0.900 | 0.063 | 14.282 | 200. | 1.21 | 1.340 | 0.0256 |
| C5 | 0.171 | 0.099 | 0.936 | 0.105 | | | | |
| MOLES | 0.041 | 0.034 | 0.006 | | 2409. | | | |
| C1 | 0.759 | 0.875 | 0.046 | 18.936 | 150. | 1.01 | 1.685 | 0.0254 |
| C5 | 0.240 | 0.124 | 0.953 | 0.130 | | | | |
| MOLES | 0.031 | 0.025 | 0.005 | | 2409. | | | |
| C1 | 0.723 | 0.823 | 0.029 | 28.228 | 100. | 0.70 | 2.259 | 0.0252 |
| C5 | 0.276 | 0.176 | 0.970 | 0.181 | | | | |
| MOLES | 0.020 | 0.016 | 0.003 | | 2409. | | | |
| C1 | 0.673 | 0.785 | 0.022 | 35.184 | 80. | 0.54 | 2.609 | 0.0251 |
| C5 | 0.326 | 0.214 | 0.977 | 0.219 | | | | |
| MOLES | 0.016 | 0.013 | 0.003 | | 2409. | | | |
| C1 | 0.644 | 0.720 | 0.015 | 46.751 | 60. | 0.31 | 3.085 | 0.0250 |
| C5 | 0.355 | 0.279 | 0.984 | 0.284 | | | | |
| MOLES | 0.011 | 0.010 | 0.001 | | 2409. | | | |

ZKATZ ITER = 0

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.615 | 0.615 | 0.000 | 1.000 | 40. | 0.00 | 3.901 | 0.0000 |
| C5 | 0.384 | 0.384 | 0.000 | 1.000 | | | | |
| MOLES | 0.006 | 0.006 | 0.000 | | 2409. | | | |

## TABLE E-8

RUN NO. 11, METHANE AND N-PENTANE AT 160 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------- PURE COMPONENT DATA -------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

--------------- SIMULATED DEPLETION PERFORMANCE ---------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.882 | 0.882 | 0.000 | 1.000 | 2500. | 0.00 | 0.093 | 0.0000 |
| C5 | 0.118 | 0.118 | 0.000 | 1.000 | | | | |
| MOLES | 0.472 | 0.472 | 0.000 | | 2278. | | | |
| C1 | 0.881 | 0.881 | 0.000 | 1.000 | 2250. | 0.00 | 0.103 | 0.0000 |
| C5 | 0.117 | 0.117 | 0.000 | 1.000 | | | | |
| MOLES | 0.426 | 0.426 | 0.000 | | 2278. | | | |
| C1 | 0.881 | 0.881 | 0.000 | 1.000 | 2000. | 0.00 | 0.116 | 0.0000 |
| C5 | 0.117 | 0.117 | 0.000 | 1.000 | | | | |
| MOLES | 0.377 | 0.377 | 0.000 | | 2278. | | | |
| C1 | 0.881 | 0.891 | 0.477 | 1.865 | 1750. | 1.48 | 0.139 | 0.0386 |
| C5 | 0.117 | 0.108 | 0.522 | 0.208 | | | | |
| MOLES | 0.326 | 0.318 | 0.008 | | 2278. | | | |
| C1 | 0.880 | 0.896 | 0.407 | 2.203 | 1500. | 1.90 | 0.169 | 0.0356 |
| C5 | 0.119 | 0.103 | 0.592 | 0.173 | | | | |
| MOLES | 0.275 | 0.265 | 0.010 | | 2278. | | | |
| C1 | 0.877 | 0.897 | 0.339 | 2.641 | 1250. | 1.75 | 0.208 | 0.0333 |
| C5 | 0.122 | 0.102 | 0.660 | 0.155 | | | | |
| MOLES | 0.225 | 0.216 | 0.009 | | 2278. | | | |
| C1 | 0.873 | 0.896 | 0.272 | 3.290 | 1000. | 1.50 | 0.267 | 0.0314 |
| C5 | 0.126 | 0.103 | 0.727 | 0.142 | | | | |
| MOLES | 0.177 | 0.168 | 0.008 | | 2278. | | | |

## TABLE E-8    (CONT.)

RUN NO. 11, METHANE AND N-PENTANE AT 160 F.

---------------- SIMULATED DEPLETION PERFORMANCE ----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.866 | 0.891 | 0.217 | 4.091 | 800. | 1.17 | 0.336 | 0.0302 |
| C5 | 0.133 | 0.108 | 0.782 | 0.138 | | | | |
| MOLES | 0.138 | 0.132 | 0.006 | | 2278. | | | |
| C1 | 0.859 | 0.879 | 0.162 | 5.417 | 600. | 0.68 | 0.445 | 0.0290 |
| C5 | 0.140 | 0.120 | 0.837 | 0.144 | | | | |
| MOLES | 0.101 | 0.097 | 0.003 | | 2278. | | | |
| C1 | 0.852 | 0.852 | 0.000 | 1.000 | 400. | 0.00 | 0.640 | 0.0000 |
| C5 | 0.147 | 0.147 | 0.000 | 1.000 | | | | |
| MOLES | 0.064 | 0.064 | 0.000 | | 2278. | | | |
| C1 | 0.852 | 0.852 | 0.000 | 1.000 | 200. | 0.00 | 1.324 | 0.0000 |
| C5 | 0.147 | 0.147 | 0.000 | 1.000 | | | | |
| MOLES | 0.031 | 0.031 | 0.000 | | 2278. | | | |
| C1 | 0.852 | 0.852 | 0.000 | 1.000 | 150. | 0.00 | 1.781 | 0.0000 |
| C5 | 0.147 | 0.147 | 0.000 | 1.000 | | | | |
| MOLES | 0.023 | 0.023 | 0.000 | | 2278. | | | |
| C1 | 0.852 | 0.852 | 0.000 | 1.000 | 100. | 0.00 | 2.693 | 0.0000 |
| C5 | 0.147 | 0.147 | 0.000 | 1.000 | | | | |
| MOLES | 0.015 | 0.015 | 0.000 | | 2278. | | | |

## TABLE E-9

RUN NO. 12, METHANE AND N-PENTANE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------ PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.927 | 0.927 | 0.000 | 1.000 | 2500. | 0.00 | 0.090 | 0.0000 |
| C5 | 0.073 | 0.073 | 0.000 | 1.000 | | | | |
| MOLES | 0.547 | 0.547 | 0.000 | | 2409. | | | |
| C1 | 0.926 | 0.926 | 0.000 | 1.000 | 2250. | 0.00 | 0.100 | 0.0000 |
| C5 | 0.072 | 0.072 | 0.000 | 1.000 | | | | |
| MOLES | 0.495 | 0.495 | 0.000 | | 2409. | | | |
| C1 | 0.926 | 0.926 | 0.000 | 1.000 | 2000. | 0.00 | 0.113 | 0.0000 |
| C5 | 0.072 | 0.072 | 0.000 | 1.000 | | | | |
| MOLES | 0.438 | 0.438 | 0.000 | | 2409. | | | |
| C1 | 0.926 | 0.940 | 0.513 | 1.831 | 1750. | 2.17 | 0.139 | 0.0355 |
| C5 | 0.072 | 0.059 | 0.486 | 0.121 | | | | |
| MOLES | 0.376 | 0.362 | 0.014 | | 2409. | | | |
| C1 | 0.924 | 0.945 | 0.446 | 2.116 | 1500. | 2.47 | 0.169 | 0.0331 |
| C5 | 0.075 | 0.054 | 0.553 | 0.098 | | | | |
| MOLES | 0.316 | 0.300 | 0.015 | | 2409. | | | |
| C1 | 0.920 | 0.949 | 0.379 | 2.502 | 1250. | 2.50 | 0.212 | 0.0312 |
| C5 | 0.079 | 0.050 | 0.620 | 0.081 | | | | |
| MOLES | 0.258 | 0.242 | 0.015 | | 2409. | | | |
| C1 | 0.914 | 0.951 | 0.309 | 3.072 | 1000. | 2.41 | 0.276 | 0.0296 |
| C5 | 0.085 | 0.048 | 0.690 | 0.070 | | | | |
| MOLES | 0.202 | 0.187 | 0.014 | | 2409. | | | |

## TABLE E-9 (CONT.)

RUN NO. 12, METHANE AND N-PENTANE AT 100 F.

---------------- SIMULATED DEPLETION PERFORMANCE ----------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|--------|-------|--------|--------|-------|---------|--------|--------|
| C1 | 0.904 | 0.951 | 0.251 | 3.779 | 800. | 2.24 | 0.355 | 0.0284 |
| C5 | 0.095 | 0.048 | 0.748 | 0.065 | | | | |
| MOLES | 0.159 | 0.146 | 0.013 | | 2409. | | | |
| C1 | 0.891 | 0.947 | 0.191 | 4.951 | 600. | 2.00 | 0.482 | 0.0274 |
| C5 | 0.108 | 0.052 | 0.808 | 0.064 | | | | |
| MOLES | 0.118 | 0.107 | 0.011 | | 2409. | | | |
| C1 | 0.872 | 0.937 | 0.128 | 7.288 | 400. | 1.65 | 0.721 | 0.0264 |
| C5 | 0.127 | 0.062 | 0.871 | 0.071 | | | | |
| MOLES | 0.079 | 0.069 | 0.009 | | 2409. | | | |
| C1 | 0.839 | 0.900 | 0.063 | 14.282 | 200. | 1.01 | 1.340 | 0.0256 |
| C5 | 0.160 | 0.099 | 0.936 | 0.105 | | | | |
| MOLES | 0.039 | 0.034 | 0.005 | | 2409. | | | |
| C1 | 0.779 | 0.875 | 0.046 | 18.936 | 150. | 0.81 | 1.685 | 0.0254 |
| C5 | 0.220 | 0.124 | 0.953 | 0.130 | | | | |
| MOLES | 0.030 | 0.025 | 0.004 | | 2409. | | | |
| C1 | 0.748 | 0.823 | 0.029 | 28.228 | 100. | 0.50 | 2.259 | 0.0252 |
| C5 | 0.251 | 0.176 | 0.970 | 0.181 | | | | |
| MOLES | 0.019 | 0.016 | 0.002 | | 2409. | | | |
| C1 | 0.709 | 0.785 | 0.022 | 35.184 | 80. | 0.35 | 2.609 | 0.0251 |
| C5 | 0.290 | 0.214 | 0.977 | 0.219 | | | | |
| MOLES | 0.015 | 0.013 | 0.001 | | 2409. | | | |
| C1 | 0.688 | 0.720 | 0.015 | 46.751 | 60. | 0.12 | 3.085 | 0.0250 |
| C5 | 0.311 | 0.279 | 0.984 | 0.284 | | | | |
| MOLES | 0.010 | 0.010 | 0.000 | | 2409. | | | |
| C1 | 0.674 | 0.674 | 0.000 | 1.000 | 40. | 0.00 | 4.303 | 0.0000 |
| C5 | 0.325 | 0.325 | 0.000 | 1.000 | | | | |
| MOLES | 0.006 | 0.006 | 0.000 | | 2409. | | | |

## TABLE E-10

METHANE, PROPANE, AND N-BUTANE MIXTURE AT 100 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

-------------------- PURE COMPONENT DATA --------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|---|---|---|---|---|---|---|---|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C3 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 0.153 | 6.540 |
| C4 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 0.195 | 6.770 |

-------------------- SIMULATED DEPLETION PERFORMANCE --------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|---|---|---|---|---|---|---|---|---|
| C1 | 0.700 | 0.700 | 0.000 | 1.000 | 1750. | 0.00 | 0.073 | 0.0000 |
| C3 | 0.180 | 0.180 | 0.000 | 1.000 | | | | |
| C4 | 0.120 | 0.120 | 0.000 | 1.000 | | | | |
| MOLES | 0.518 | 0.518 | 0.000 | | 1724. | | | |
| C1 | 0.699 | 0.705 | 0.501 | 1.407 | 1650. | 2.06 | 0.080 | 0.0473 |
| C3 | 0.179 | 0.177 | 0.267 | 0.663 | | | | |
| C4 | 0.119 | 0.117 | 0.231 | 0.506 | | | | |
| MOLES | 0.484 | 0.471 | 0.013 | | 1718. | | | |
| C1 | 0.699 | 0.707 | 0.450 | 1.570 | 1600. | 2.35 | 0.083 | 0.0434 |
| C3 | 0.180 | 0.176 | 0.287 | 0.615 | | | | |
| C4 | 0.120 | 0.115 | 0.262 | 0.440 | | | | |
| MOLES | 0.466 | 0.450 | 0.015 | | 1718. | | | |
| C1 | 0.699 | 0.723 | 0.396 | 1.824 | 1500. | 5.12 | 0.096 | 0.0405 |
| C3 | 0.180 | 0.170 | 0.307 | 0.553 | | | | |
| C4 | 0.120 | 0.106 | 0.295 | 0.360 | | | | |
| MOLES | 0.424 | 0.390 | 0.034 | | 1718. | | | |
| C1 | 0.696 | 0.755 | 0.326 | 2.317 | 1250. | 8.76 | 0.137 | 0.0380 |
| C3 | 0.181 | 0.156 | 0.335 | 0.468 | | | | |
| C4 | 0.121 | 0.087 | 0.338 | 0.257 | | | | |
| MOLES | 0.333 | 0.274 | 0.058 | | 1718. | | | |
| C1 | 0.680 | 0.771 | 0.273 | 2.826 | 1000. | 9.26 | 0.194 | 0.0365 |
| C3 | 0.187 | 0.150 | 0.353 | 0.426 | | | | |
| C4 | 0.131 | 0.077 | 0.373 | 0.206 | | | | |
| MOLES | 0.259 | 0.198 | 0.060 | | 1719. | | | |

## TABLE E-10 (CONT.)

METHANE, PROPANE, AND N-BUTANE MIXTURE AT 100 F.

```
-------------- SIMULATED DEPLETION PERFORMANCE --------------
        SYSTEM   VAPOR    LIQUID    K      P, PK   LIQ   VAPOR    LIQUID
COMP    COMP     COMP     COMP    VALUE    PSIA  VOL %   CF/LB    CF/LB
----    -----    -----    -----   -----    ----  ----    -----    -----
```

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.654 | 0.771 | 0.249 | 3.090 | 900. | 8.84 | 0.222 | 0.0358 |
| C3 | 0.198 | 0.152 | 0.359 | 0.422 | | | | |
| C4 | 0.146 | 0.076 | 0.390 | 0.195 | | | | |
| MOLES | 0.231 | 0.174 | 0.057 | | 1718. | | | |
| C1 | 0.641 | 0.766 | 0.224 | 3.415 | 800. | 8.24 | 0.255 | 0.0351 |
| C3 | 0.203 | 0.155 | 0.365 | 0.425 | | | | |
| C4 | 0.154 | 0.077 | 0.410 | 0.189 | | | | |
| MOLES | 0.205 | 0.151 | 0.053 | | 1718. | | | |
| C1 | 0.624 | 0.758 | 0.197 | 3.832 | 700. | 7.52 | 0.295 | 0.0344 |
| C3 | 0.210 | 0.160 | 0.368 | 0.436 | | | | |
| C4 | 0.164 | 0.080 | 0.433 | 0.186 | | | | |
| MOLES | 0.179 | 0.130 | 0.048 | | 1717. | | | |
| C1 | 0.605 | 0.743 | 0.169 | 4.365 | 600. | 6.68 | 0.345 | 0.0337 |
| C3 | 0.217 | 0.169 | 0.369 | 0.458 | | | | |
| C4 | 0.176 | 0.086 | 0.461 | 0.188 | | | | |
| MOLES | 0.153 | 0.110 | 0.043 | | 1715. | | | |
| C1 | 0.582 | 0.721 | 0.139 | 5.158 | 500. | 5.73 | 0.410 | 0.0330 |
| C3 | 0.225 | 0.181 | 0.365 | 0.496 | | | | |
| C4 | 0.192 | 0.096 | 0.494 | 0.195 | | | | |
| MOLES | 0.127 | 0.091 | 0.036 | | 1711. | | | |
| C1 | 0.554 | 0.687 | 0.108 | 6.318 | 400. | 4.62 | 0.499 | 0.0323 |
| C3 | 0.234 | 0.198 | 0.354 | 0.559 | | | | |
| C4 | 0.211 | 0.113 | 0.536 | 0.211 | | | | |
| MOLES | 0.101 | 0.072 | 0.029 | | 1704. | | | |
| C1 | 0.520 | 0.632 | 0.076 | 8.250 | 300. | 3.26 | 0.630 | 0.0314 |
| C3 | 0.243 | 0.221 | 0.329 | 0.673 | | | | |
| C4 | 0.236 | 0.145 | 0.594 | 0.244 | | | | |
| MOLES | 0.074 | 0.054 | 0.020 | | 1689. | | | |
| C1 | 0.479 | 0.534 | 0.044 | 12.115 | 200. | 1.35 | 0.848 | 0.0305 |
| C3 | 0.251 | 0.248 | 0.273 | 0.910 | | | | |
| C4 | 0.269 | 0.216 | 0.682 | 0.317 | | | | |
| MOLES | 0.044 | 0.036 | 0.008 | | 1657. | | | |

## TABLE E-11 (CONT.)

METHANE, PROPANE, AND N-BUTANE MIXTURE AT 160 F.

-------------- SIMULATED DEPLETION PERFORMANCE --------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.534 | 0.588 | 0.201 | 2.924 | 1000. | 6.46 | 0.157 | 0.0396 |
| C3 | 0.276 | 0.257 | 0.394 | 0.651 | | | | |
| C4 | 0.189 | 0.154 | 0.404 | 0.382 | | | | |
| MOLES | 0.236 | 0.199 | 0.036 | | 1443. | | | |
| C1 | 0.527 | 0.584 | 0.180 | 3.242 | 900. | 5.80 | 0.181 | 0.0389 |
| C3 | 0.278 | 0.259 | 0.395 | 0.656 | | | | |
| C4 | 0.193 | 0.156 | 0.424 | 0.367 | | | | |
| MOLES | 0.207 | 0.173 | 0.033 | | 1444. | | | |
| C1 | 0.519 | 0.573 | 0.158 | 3.625 | 800. | 4.71 | 0.207 | 0.0381 |
| C3 | 0.281 | 0.264 | 0.393 | 0.673 | | | | |
| C4 | 0.199 | 0.161 | 0.448 | 0.360 | | | | |
| MOLES | 0.178 | 0.151 | 0.026 | | 1444. | | | |
| C1 | 0.510 | 0.555 | 0.135 | 4.105 | 700. | 3.31 | 0.237 | 0.0373 |
| C3 | 0.283 | 0.271 | 0.386 | 0.703 | | | | |
| C4 | 0.205 | 0.172 | 0.478 | 0.361 | | | | |
| MOLES | 0.150 | 0.131 | 0.018 | | 1445. | | | |
| C1 | 0.502 | 0.528 | 0.111 | 4.736 | 600. | 1.66 | 0.275 | 0.0365 |
| C3 | 0.286 | 0.280 | 0.373 | 0.751 | | | | |
| C4 | 0.211 | 0.190 | 0.515 | 0.370 | | | | |
| MOLES | 0.121 | 0.111 | 0.009 | | 1445. | | | |
| C1 | 0.496 | 0.496 | 0.000 | 1.000 | 500. | 0.00 | 0.325 | 0.0000 |
| C3 | 0.287 | 0.287 | 0.000 | 1.000 | | | | |
| C4 | 0.216 | 0.216 | 0.000 | 1.000 | | | | |
| MOLES | 0.092 | 0.092 | 0.000 | | 1445. | | | |
| C1 | 0.496 | 0.496 | 0.000 | 1.000 | 400. | 0.00 | 0.427 | 0.0000 |
| C3 | 0.287 | 0.287 | 0.000 | 1.000 | | | | |
| C4 | 0.216 | 0.216 | 0.000 | 1.000 | | | | |
| MOLES | 0.070 | 0.070 | 0.000 | | 1445. | | | |
| C1 | 0.496 | 0.496 | 0.000 | 1.000 | 300. | 0.00 | 0.595 | 0.0000 |
| C3 | 0.287 | 0.287 | 0.000 | 1.000 | | | | |
| C4 | 0.216 | 0.216 | 0.000 | 1.000 | | | | |
| MOLES | 0.050 | 0.050 | 0.000 | | 1445. | | | |

## TABLE E-12

METHANE, PROPANE, AND N-PENTANE MIXTURE AT 160 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------ PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C3 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 0.153 | 6.540 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.238 | 7.030 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.675 | 0.675 | 0.000 | 1.000 | 2000. | 0.00 | 0.073 | 0.0000 |
| C3 | 0.195 | 0.195 | 0.000 | 1.000 | | | | |
| C5 | 0.130 | 0.130 | 0.000 | 1.000 | | | | |
| MOLES | 0.471 | 0.471 | 0.000 | | 1880. | | | |
| C1 | 0.674 | 0.689 | 0.441 | 1.559 | 1750. | 4.78 | 0.088 | 0.0447 |
| C3 | 0.194 | 0.190 | 0.273 | 0.695 | | | | |
| C5 | 0.129 | 0.120 | 0.284 | 0.423 | | | | |
| MOLES | 0.407 | 0.380 | 0.026 | | 1853. | | | |
| C1 | 0.672 | 0.722 | 0.334 | 2.160 | 1500. | 8.97 | 0.120 | 0.0381 |
| C3 | 0.195 | 0.180 | 0.297 | 0.606 | | | | |
| C5 | 0.131 | 0.096 | 0.367 | 0.263 | | | | |
| MOLES | 0.337 | 0.285 | 0.052 | | 1853. | | | |
| C1 | 0.662 | 0.738 | 0.280 | 2.631 | 1250. | 9.74 | 0.159 | 0.0361 |
| C3 | 0.198 | 0.177 | 0.306 | 0.579 | | | | |
| C5 | 0.138 | 0.083 | 0.413 | 0.202 | | | | |
| MOLES | 0.276 | 0.220 | 0.056 | | 1853. | | | |
| C1 | 0.645 | 0.739 | 0.230 | 3.212 | 1000. | 8.89 | 0.210 | 0.0344 |
| C3 | 0.203 | 0.180 | 0.306 | 0.587 | | | | |
| C5 | 0.150 | 0.080 | 0.463 | 0.173 | | | | |
| MOLES | 0.219 | 0.168 | 0.050 | | 1856. | | | |
| C1 | 0.621 | 0.729 | 0.185 | 3.923 | 800. | 7.69 | 0.269 | 0.0330 |
| C3 | 0.209 | 0.187 | 0.299 | 0.626 | | | | |
| C5 | 0.169 | 0.083 | 0.514 | 0.161 | | | | |
| MOLES | 0.175 | 0.131 | 0.043 | | 1857. | | | |

## TABLE E-12 (CONT.)

METHANE, PROPANE, AND N-PENTANE MIXTURE AT 160 F.

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-------------- SIMULATED DEPLETION PERFORMANCE --------------
```

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|-------------|------------|-------------|---------|------------|-----------|-------------|--------------|
| C1 | 0.594 | 0.706 | 0.138 | 5.104 | 600. | 6.18 | 0.358 | 0.0314 |
| C3 | 0.215 | 0.199 | 0.278 | 0.715 | | | | |
| C5 | 0.190 | 0.093 | 0.582 | 0.161 | | | | |
| MOLES | 0.131 | 0.097 | 0.034 | | 1854. | | | |
| C1 | 0.556 | 0.687 | 0.113 | 6.047 | 500. | 5.37 | 0.424 | 0.0306 |
| C3 | 0.220 | 0.208 | 0.261 | 0.795 | | | | |
| C5 | 0.222 | 0.104 | 0.624 | 0.167 | | | | |
| MOLES | 0.110 | 0.030 | 0.029 | | 1848. | | | |
| C1 | 0.531 | 0.659 | 0.088 | 7.463 | 400. | 4.46 | 0.515 | 0.0298 |
| C3 | 0.222 | 0.218 | 0.237 | 0.921 | | | | |
| C5 | 0.245 | 0.122 | 0.674 | 0.181 | | | | |
| MOLES | 0.088 | 0.063 | 0.024 | | 1838. | | | |
| C1 | 0.500 | 0.616 | 0.062 | 9.824 | 300. | 3.41 | 0.651 | 0.0290 |
| C3 | 0.223 | 0.229 | 0.201 | 1.137 | | | | |
| C5 | 0.276 | 0.153 | 0.735 | 0.208 | | | | |
| MOLES | 0.066 | 0.047 | 0.018 | | 1820. | | | |
| C1 | 0.460 | 0.544 | 0.037 | 14.546 | 200. | 2.03 | 0.882 | 0.0281 |
| C3 | 0.221 | 0.236 | 0.149 | 1.579 | | | | |
| C5 | 0.317 | 0.218 | 0.813 | 0.269 | | | | |
| MOLES | 0.042 | 0.031 | 0.010 | | 1788. | | | |
| C1 | 0.414 | 0.482 | 0.025 | 19.259 | 150. | 1.18 | 1.072 | 0.0276 |
| C3 | 0.213 | 0.231 | 0.114 | 2.024 | | | | |
| C5 | 0.371 | 0.285 | 0.860 | 0.332 | | | | |
| MOLES | 0.030 | 0.023 | 0.006 | | 1762. | | | |
| ZKATZ ITER = 0 | | | | | | | | |
| C1 | 0.386 | 0.386 | 0.000 | 1.000 | 100. | 0.00 | 1.389 | 0.0000 |
| C3 | 0.206 | 0.206 | 0.000 | 1.000 | | | | |
| C5 | 0.406 | 0.406 | 0.000 | 1.000 | | | | |
| MOLES | 0.016 | 0.016 | 0.000 | | 1762. | | | |

## TABLE E-13

METHANE, PROPANE, AND N-PENTANE MIXTURE AT 220 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------ PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|------|------|------|------|------|------|------|
| C1 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 0.000 | 5.860 |
| C3 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 0.153 | 6.540 |
| C5 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 0.239 | 7.030 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.500 | 0.500 | 0.000 | 1.000 | 1500. | 0.00 | 0.080 | 0.0000 |
| C3 | 0.300 | 0.300 | 0.000 | 1.000 | | | | |
| C5 | 0.200 | 0.200 | 0.000 | 1.000 | | | | |
| MOLES | 0.346 | 0.346 | 0.000 | | 1469. | | | |
| C1 | 0.500 | 0.558 | 0.324 | 1.719 | 1400. | 19.22 | 0.106 | 0.0507 |
| C3 | 0.299 | 0.280 | 0.359 | 0.780 | | | | |
| C5 | 0.199 | 0.161 | 0.316 | 0.510 | | | | |
| MOLES | 0.315 | 0.229 | 0.086 | | 1469. | | | |
| C1 | 0.494 | 0.563 | 0.255 | 2.202 | 1300. | 14.54 | 0.120 | 0.0434 |
| C3 | 0.301 | 0.281 | 0.371 | 0.758 | | | | |
| C5 | 0.203 | 0.155 | 0.372 | 0.416 | | | | |
| MOLES | 0.288 | 0.217 | 0.070 | | 1467. | | | |
| C1 | 0.487 | 0.565 | 0.236 | 2.388 | 1250. | 13.81 | 0.127 | 0.0420 |
| C3 | 0.303 | 0.282 | 0.372 | 0.757 | | | | |
| C5 | 0.208 | 0.152 | 0.390 | 0.390 | | | | |
| MOLES | 0.275 | 0.207 | 0.067 | | 1466. | | | |
| C1 | 0.484 | 0.565 | 0.221 | 2.557 | 1200. | 13.20 | 0.135 | 0.0410 |
| C3 | 0.304 | 0.283 | 0.372 | 0.761 | | | | |
| C5 | 0.211 | 0.150 | 0.406 | 0.370 | | | | |
| MOLES | 0.263 | 0.197 | 0.065 | | 1465. | | | |
| C1 | 0.480 | 0.562 | 0.196 | 2.863 | 1100. | 11.80 | 0.150 | 0.0394 |
| C3 | 0.305 | 0.287 | 0.368 | 0.780 | | | | |
| C5 | 0.213 | 0.150 | 0.435 | 0.345 | | | | |
| MOLES | 0.238 | 0.180 | 0.058 | | 1465. | | | |

## TABLE E-13 (CONT.)

METHANE, PROPANE, AND N-PENTANE MIXTURE AT 220 F.

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|-------------|------------|-------------|---------|---------|--------------|-------------|--------------|
| C1 | 0.471 | 0.557 | 0.175 | 3.178 | 1000. | 10.69 | 0.168 | 0.0384 |
| C3 | 0.307 | 0.291 | 0.363 | 0.803 | | | | |
| C5 | 0.220 | 0.151 | 0.461 | 0.327 | | | | |
| MOLES | 0.215 | 0.161 | 0.053 | | 1465. | | | |
| C1 | 0.462 | 0.547 | 0.155 | 3.522 | 900. | 9.33 | 0.189 | 0.0374 |
| C3 | 0.309 | 0.296 | 0.354 | 0.836 | | | | |
| C5 | 0.228 | 0.155 | 0.489 | 0.317 | | | | |
| MOLES | 0.191 | 0.144 | 0.046 | | 1466. | | | |
| C1 | 0.451 | 0.534 | 0.135 | 3.948 | 800. | 7.88 | 0.213 | 0.0364 |
| C3 | 0.310 | 0.302 | 0.342 | 0.883 | | | | |
| C5 | 0.237 | 0.163 | 0.521 | 0.312 | | | | |
| MOLES | 0.167 | 0.128 | 0.039 | | 1467. | | | |
| C1 | 0.440 | 0.516 | 0.114 | 4.492 | 700. | 6.34 | 0.242 | 0.0353 |
| C3 | 0.312 | 0.308 | 0.326 | 0.947 | | | | |
| C5 | 0.247 | 0.174 | 0.559 | 0.312 | | | | |
| MOLES | 0.143 | 0.111 | 0.031 | | 1467. | | | |
| C1 | 0.427 | 0.493 | 0.094 | 5.214 | 600. | 4.74 | 0.279 | 0.0342 |
| C3 | 0.312 | 0.314 | 0.302 | 1.038 | | | | |
| C5 | 0.259 | 0.191 | 0.602 | 0.318 | | | | |
| MOLES | 0.119 | 0.095 | 0.023 | | 1465. | | | |
| C1 | 0.414 | 0.463 | 0.074 | 6.223 | 500. | 3.02 | 0.327 | 0.0332 |
| C3 | 0.312 | 0.318 | 0.271 | 1.170 | | | | |
| C5 | 0.273 | 0.218 | 0.653 | 0.333 | | | | |
| MOLES | 0.094 | 0.079 | 0.015 | | 1461. | | | |
| C1 | 0.401 | 0.423 | 0.054 | 7.735 | 400. | 1.14 | 0.391 | 0.0320 |
| C3 | 0.310 | 0.315 | 0.229 | 1.375 | | | | |
| C5 | 0.287 | 0.260 | 0.715 | 0.363 | | | | |
| MOLES | 0.069 | 0.063 | 0.005 | | 1454. | | | |
| C1 | 0.393 | 0.393 | 0.000 | 1.000 | 300. | 0.00 | 0.514 | 0.0000 |
| C3 | 0.308 | 0.308 | 0.000 | 1.000 | | | | |
| C5 | 0.297 | 0.297 | 0.000 | 1.000 | | | | |
| MOLES | 0.046 | 0.046 | 0.000 | | 1454. | | | |

## TABLE E-14

METHANE, PROPANE, N-DECANE MIXTURE AT 280 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------------ PURE COMPONENT DATA ------------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|-----------------|---------|----------|----------|-------|--------------|--------------|
| C1   | 16.042          | 669.7   | 1.590    | 343.13   | 0.288 | 0.000        | 5.860        |
| C3   | 44.094          | 616.3   | 3.210    | 665.68   | 0.276 | 0.153        | 6.540        |
| C10  | 142.276         | 304.0   | 9.660    | 1111.70  | 0.246 | 0.486        | 8.180        |

------------------------------ SIMULATED DEPLETION PERFORMANCE ------------------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PSIA | PK LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|-------------|------------|-------------|---------|---------|--------------|-------------|--------------|
| C1   | 0.875       | 0.911      | 0.822       | 1.1086  | 3750.   | 41.51        | 0.095       | 0.0713       |
| C3   | 0.075       | 0.059      | 0.096       | 0.6191  |         |              |             |              |
| C10  | 0.050       | 0.028      | 0.080       | 0.3509  |         |              |             |              |
| MOLES | 0.486      | 0.285      | 0.200       |         | 3915.   |              |             |              |
| C1   | 0.874       | 0.903      | 0.735       | 1.2294  | 3500.   | 18.30        | 0.099       | 0.0581       |
| C3   | 0.075       | 0.065      | 0.120       | 0.5436  |         |              |             |              |
| C10  | 0.050       | 0.030      | 0.144       | 0.2121  |         |              |             |              |
| MOLES | 0.462      | 0.378      | 0.083       |         | 3914.   |              |             |              |
| C1   | 0.873       | 0.905      | 0.672       | 1.3462  | 3250.   | 14.47        | 0.107       | 0.0511       |
| C3   | 0.075       | 0.066      | 0.130       | 0.5108  |         |              |             |              |
| C10  | 0.051       | 0.027      | 0.196       | 0.1418  |         |              |             |              |
| MOLES | 0.434      | 0.371      | 0.063       |         | 3912.   |              |             |              |
| C1   | 0.871       | 0.908      | 0.618       | 1.4699  | 3000.   | 13.10        | 0.118       | 0.0461       |
| C3   | 0.076       | 0.067      | 0.135       | 0.4961  |         |              |             |              |
| C10  | 0.052       | 0.024      | 0.246       | 0.0978  |         |              |             |              |
| MOLES | 0.405      | 0.349      | 0.055       |         | 3909.   |              |             |              |
| C1   | 0.868       | 0.914      | 0.518       | 1.7638  | 2500.   | 11.66        | 0.147       | 0.0391       |
| C3   | 0.076       | 0.068      | 0.137       | 0.5001  |         |              |             |              |
| C10  | 0.054       | 0.016      | 0.343       | 0.0485  |         |              |             |              |
| MOLES | 0.345      | 0.298      | 0.047       |         | 3906.   |              |             |              |
| C1   | 0.860       | 0.916      | 0.421       | 2.1752  | 2000.   | 10.18        | 0.188       | 0.0343       |
| C3   | 0.078       | 0.071      | 0.131       | 0.5437  |         |              |             |              |
| C10  | 0.061       | 0.012      | 0.447       | 0.0273  |         |              |             |              |
| MOLES | 0.281      | 0.242      | 0.038       |         | 3903.   |              |             |              |

## TABLE E-14   (CONT.)

METHANE, PROPANE, N-DECANE MIXTURE AT 280 F.

--------------- SIMULATED DEPLETION PERFORMANCE ---------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1   | 0.847 | 0.910 | 0.321 | 2.8367 | 1500. | 8.38 | 0.248 | 0.0308 |
| C3   | 0.079 | 0.075 | 0.116 | 0.6444 |       |      |       |        |
| C10  | 0.072 | 0.013 | 0.562 | 0.0245 |       |      |       |        |
| MOLES | 0.215 | 0.184 | 0.030 |      | 3926. |      |       |        |
| C1   | 0.828 | 0.905 | 0.218 | 4.1451 | 1000. | 7.20 | 0.373 | 0.0282 |
| C3   | 0.081 | 0.079 | 0.092 | 0.8592 |       |      |       |        |
| C10  | 0.090 | 0.014 | 0.688 | 0.0215 |       |      |       |        |
| MOLES | 0.147 | 0.123 | 0.024 |      | 3941. |      |       |        |
| C1   | 0.793 | 0.902 | 0.176 | 5.1217 | 800. | 6.81 | 0.467 | 0.0273 |
| C3   | 0.081 | 0.082 | 0.079 | 1.0258 |       |      |       |        |
| C10  | 0.125 | 0.015 | 0.743 | 0.0209 |       |      |       |        |
| MOLES | 0.120 | 0.098 | 0.022 |      | 3942. |      |       |        |
| C1   | 0.768 | 0.897 | 0.133 | 6.7463 | 600. | 6.43 | 0.620 | 0.0265 |
| C3   | 0.081 | 0.085 | 0.065 | 1.3078 |       |      |       |        |
| C10  | 0.149 | 0.017 | 0.801 | 0.0212 |       |      |       |        |
| MOLES | 0.093 | 0.073 | 0.020 |      | 3939. |      |       |        |
| C1   | 0.731 | 0.890 | 0.089 | 9.9912 | 400. | 6.04 | 0.915 | 0.0257 |
| C3   | 0.080 | 0.088 | 0.047 | 1.8781 |       |      |       |        |
| C10  | 0.187 | 0.020 | 0.863 | 0.0237 |       |      |       |        |
| MOLES | 0.067 | 0.048 | 0.018 |      | 3929. |      |       |        |
| C1   | 0.668 | 0.873 | 0.044 | 19.7175 | 200. | 5.55 | 1.717 | 0.0250 |
| C3   | 0.077 | 0.094 | 0.026 | 3.6011 |       |      |       |        |
| C10  | 0.253 | 0.032 | 0.929 | 0.0347 |       |      |       |        |
| MOLES | 0.040 | 0.024 | 0.016 |      | 3906. |      |       |        |
| C1   | 0.536 | 0.844 | 0.021 | 39.1565 | 100. | 5.21 | 3.027 | 0.0246 |
| C3   | 0.066 | 0.098 | 0.013 | 7.0540 |       |      |       |        |
| C10  | 0.397 | 0.056 | 0.964 | 0.0590 |       |      |       |        |
| MOLES | 0.027 | 0.012 | 0.015 |      | 3874. |      |       |        |
| C1   | 0.384 | 0.794 | 0.010 | 77.9953 | 50. | 4.90 | 4.885 | 0.0245 |
| C3   | 0.051 | 0.099 | 0.007 | 13.9564 |      |      |       |        |
| C10  | 0.564 | 0.106 | 0.982 | 0.1086 |       |      |       |        |
| MOLES | 0.020 | 0.006 | 0.014 |      | 3838. |      |       |        |

## TABLE E-15

METHANE, N-BUTANE, AND N-DECANE MIXTURE AT 280 F.
DEPLETION OF A CONSTANT VOLUME RESERVOIR BY VAPOR PRODUCTION

------------------------ PURE COMPONENT DATA ------------------------

| COMP | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | PITZER OMEGA | RIEDEL ALPHA |
|------|---------|---------|---------|---------|------|-------|-------|
| C1   | 16.042  | 669.7   | 1.590   | 343.13  | 0.288 | 0.000 | 5.860 |
| C4   | 58.120  | 550.7   | 4.080   | 765.29  | 0.274 | 0.195 | 6.770 |
| C10  | 142.276 | 304.0   | 9.660   | 1111.70 | 0.246 | 0.486 | 8.190 |

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|--------|-------|------|-------|--------|
| C1   | 0.900 | 0.907 | 0.734 | 1.2351 | 3500. | 4.53 | 0.093 | 0.0543 |
| C4   | 0.060 | 0.057 | 0.107 | 0.5401 |       |      |       |        |
| C10  | 0.040 | 0.034 | 0.158 | 0.2184 |       |      |       |        |
| MOLES | 0.465 | 0.444 | 0.020 |        | 3897. |      |       |        |
| C1   | 0.899 | 0.912 | 0.673 | 1.3544 | 3250. | 5.59 | 0.102 | 0.0480 |
| C4   | 0.060 | 0.056 | 0.115 | 0.4920 |       |      |       |        |
| C10  | 0.040 | 0.030 | 0.210 | 0.1449 |       |      |       |        |
| MOLES | 0.435 | 0.411 | 0.024 |        | 3897. |      |       |        |
| C1   | 0.899 | 0.918 | 0.621 | 1.4784 | 3000. | 6.62 | 0.114 | 0.0437 |
| C4   | 0.060 | 0.055 | 0.121 | 0.4613 |       |      |       |        |
| C10  | 0.040 | 0.025 | 0.257 | 0.0996 |       |      |       |        |
| MOLES | 0.405 | 0.377 | 0.028 |        | 3896. |      |       |        |
| C1   | 0.897 | 0.923 | 0.572 | 1.6143 | 2750. | 7.20 | 0.128 | 0.0405 |
| C4   | 0.060 | 0.055 | 0.125 | 0.4408 |       |      |       |        |
| C10  | 0.041 | 0.021 | 0.302 | 0.0696 |       |      |       |        |
| MOLES | 0.374 | 0.344 | 0.029 |        | 3895. |      |       |        |
| C1   | 0.895 | 0.927 | 0.524 | 1.7693 | 2500. | 7.40 | 0.144 | 0.0379 |
| C4   | 0.060 | 0.055 | 0.128 | 0.4279 |       |      |       |        |
| C10  | 0.043 | 0.017 | 0.346 | 0.0495 |       |      |       |        |
| MOLES | 0.342 | 0.313 | 0.029 |        | 3894. |      |       |        |
| C1   | 0.892 | 0.930 | 0.476 | 1.9522 | 2250. | 7.31 | 0.163 | 0.0357 |
| C4   | 0.061 | 0.055 | 0.130 | 0.4214 |       |      |       |        |
| C10  | 0.045 | 0.014 | 0.392 | 0.0361 |       |      |       |        |
| MOLES | 0.310 | 0.282 | 0.028 |        | 3893. |      |       |        |

## TABLE E-15   (CONT.)

METHANE, N-BUTANE, AND N-DECANE MIXTURE AT 280 F.

-------------- SIMULATED DEPLETION PERFORMANCE --------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1  | 0.888 | 0.932 | 0.428 | 2.1755 | 2000. | 7.02 | 0.185 | 0.0339 |
| C4  | 0.062 | 0.055 | 0.131 | 0.4213 | | | | |
| C10 | 0.049 | 0.012 | 0.433 | 0.0278 | | | | |
| MOLES | 0.278 | 0.251 | 0.026 | | 3892. | | | |
| C1  | 0.883 | 0.930 | 0.378 | 2.4570 | 1750. | 6.36 | 0.210 | 0.0322 |
| C4  | 0.062 | 0.056 | 0.131 | 0.4302 | | | | |
| C10 | 0.053 | 0.012 | 0.489 | 0.0264 | | | | |
| MOLES | 0.244 | 0.221 | 0.023 | | 3903. | | | |
| C1  | 0.877 | 0.928 | 0.328 | 2.8301 | 1500. | 5.84 | 0.245 | 0.0308 |
| C4  | 0.063 | 0.057 | 0.129 | 0.4464 | | | | |
| C10 | 0.059 | 0.013 | 0.542 | 0.0248 | | | | |
| MOLES | 0.211 | 0.190 | 0.021 | | 3915. | | | |
| C1  | 0.868 | 0.927 | 0.276 | 3.3506 | 1250. | 5.41 | 0.294 | 0.0295 |
| C4  | 0.064 | 0.058 | 0.124 | 0.4745 | | | | |
| C10 | 0.066 | 0.013 | 0.599 | 0.0231 | | | | |
| MOLES | 0.177 | 0.158 | 0.018 | | 3926. | | | |
| C1  | 0.857 | 0.925 | 0.224 | 4.1295 | 1000. | 5.02 | 0.369 | 0.0283 |
| C4  | 0.065 | 0.060 | 0.115 | 0.5236 | | | | |
| C10 | 0.076 | 0.014 | 0.660 | 0.0217 | | | | |
| MOLES | 0.143 | 0.126 | 0.017 | | 3936. | | | |
| C1  | 0.841 | 0.922 | 0.180 | 5.1016 | 800. | 4.73 | 0.461 | 0.0274 |
| C4  | 0.067 | 0.062 | 0.105 | 0.5916 | | | | |
| C10 | 0.091 | 0.015 | 0.713 | 0.0210 | | | | |
| MOLES | 0.116 | 0.100 | 0.015 | | 3943. | | | |
| C1  | 0.822 | 0.918 | 0.136 | 6.7208 | 600. | 4.43 | 0.611 | 0.0266 |
| C4  | 0.068 | 0.063 | 0.091 | 0.7122 | | | | |
| C10 | 0.108 | 0.016 | 0.772 | 0.0213 | | | | |
| MOLES | 0.089 | 0.074 | 0.014 | | 3946. | | | |
| C1  | 0.793 | 0.915 | 0.114 | 8.0157 | 500. | 4.28 | 0.729 | 0.0262 |
| C4  | 0.069 | 0.066 | 0.082 | 0.8119 | | | | |
| C10 | 0.136 | 0.017 | 0.803 | 0.0221 | | | | |
| MOLES | 0.075 | 0.062 | 0.013 | | 3945. | | | |

TABLE E-15   (CONT.)

METHANE, N-BUTANE, AND N-DECANE MIXTURE AT 280 F.

------------------ SIMULATED DEPLETION PERFORMANCE ------------------

| COMP | SYSTEM COMP | VAPOR COMP | LIQUID COMP | K VALUE | P, PK PSIA | LIQ VOL % | VAPOR CF/LB | LIQUID CF/LB |
|------|------|------|------|------|------|------|------|------|
| C1 | 0.772 | 0.910 | 0.091 | 9.9582 | 400. | 4.12 | 0.900 | 0.0258 |
| C4 | 0.069 | 0.069 | 0.071 | 0.9640 | | | | |
| C10 | 0.157 | 0.019 | 0.836 | 0.0238 | | | | |
| MOLES | 0.062 | 0.049 | 0.012 | | 3941. | | | |
| C1 | 0.742 | 0.903 | 0.068 | 13.1958 | 300. | 3.94 | 1.173 | 0.0254 |
| C4 | 0.069 | 0.072 | 0.059 | 1.2207 | | | | |
| C10 | 0.187 | 0.023 | 0.872 | 0.0273 | | | | |
| MOLES | 0.049 | 0.037 | 0.012 | | 3931. | | | |
| C1 | 0.699 | 0.891 | 0.045 | 19.6719 | 200. | 3.72 | 1.679 | 0.0251 |
| C4 | 0.069 | 0.076 | 0.043 | 1.7386 | | | | |
| C10 | 0.231 | 0.031 | 0.910 | 0.0349 | | | | |
| MOLES | 0.035 | 0.024 | 0.011 | | 3912. | | | |
| C1 | 0.627 | 0.880 | 0.033 | 26.1476 | 150. | 3.59 | 2.139 | 0.0249 |
| C4 | 0.066 | 0.079 | 0.035 | 2.2586 | | | | |
| C10 | 0.305 | 0.039 | 0.931 | 0.0429 | | | | |
| MOLES | 0.029 | 0.018 | 0.010 | | 3893. | | | |
| C1 | 0.570 | 0.860 | 0.022 | 39.0972 | 100. | 3.42 | 2.948 | 0.0247 |
| C4 | 0.063 | 0.083 | 0.025 | 3.3002 | | | | |
| C10 | 0.366 | 0.056 | 0.952 | 0.0592 | | | | |
| MOLES | 0.022 | 0.012 | 0.010 | | 3864. | | | |
| C1 | 0.482 | 0.806 | 0.010 | 77.9216 | 50. | 3.12 | 4.763 | 0.0245 |
| C4 | 0.057 | 0.087 | 0.013 | 6.4258 | | | | |
| C10 | 0.460 | 0.106 | 0.976 | 0.1087 | | | | |
| MOLES | 0.015 | 0.006 | 0.009 | | 3810. | | | |

APPENDIX F

CORRELATION OF CRITICAL COMPRESSIBILITY FACTORS

AND CRITICAL PRESSURES FOR BINARY MIXTURES

## F.1   Foreword

Pseudocritical properties are extensively used to correlate thermodynamic data for mixtures. Pseudocritical $Z_c$ values are useful in some corresponding states correlations, however, their relationship to true $Z_c$ values has received little attention. This appendix summarizes the results of an attempt to correlate critical pressures of binary mixtures using true $Z_c$ values. Although the procedure was not sufficiently accurate for quantitative calculations it is of some academic interest.

The procedure used was a modification of a method proposed by Chueh and Prausnitz[46]. They showed that the critical temperatures and the critical volumes of binary mixtures, and perhaps multicomponent mixtures, can be correlated by the relationships

$$T_c = \sum_i \phi_i T_{ci} + \sum_i \sum_j \phi_i \phi_j T_{cij} \qquad (F-1)$$

$$V_c = \sum_i \phi_i V_{ci} + \sum_i \sum_j \phi_i \phi_j V_{cij} \qquad (F-2)$$

where: $\phi_i$, $\phi_j$ are weighting factors which reflect the composition of the mixture,

$T_{ci}$ is the critical temperature of pure component i,

$T_{cij}$ is a correlation parameter which characterizes the effects of the i-j interactions on the critical temperature, $T_{cii} = 0$,

$V_{ci}$ is the critical volume of pure component i,

$V_{cij}$ is a correlation parameter which characterizes the effects of the i-j interactions on the critical volume, $V_{cii} = 0$.

The interaction between each binary pair is characterized by a single correlating parameter and higher order interactions

are assumed to be small and are neglected. A functional form
which used more correlating parameters would have improved the
fit, however, it would have the serious disadvantage of re-
stricting the method to those systems for which there is ex-
perimental data. The strength of Equations F-1 and F-2 lies
in the fact that the correlation parameter for each binary
system can usually be related to some other properties of the
pure components. This makes it possible to estimate parame-
ters for the systems for which there is no experimental data.

The chief disadvantage of Equations F-1 and F-2 is that
the i-j interactions are assumed to be symmetric with respect
to the weighting. Chueh and Prausnitz tried several weight-
ings and found that the surface fraction

$$\phi_i = x_i V_{ci}^{2/3} / \sum_i x_i V_{ci}^{2/3} \tag{F-3}$$

gave a satisfactory representation of the experimental data.
They correlated critical pressures using Equations F-1, F-2
and F-3 in conjunction with a modified Redlich-Kwong equation
of state.

The object of this investigation was to see if true $Z_c$
values could be easily correlated. If they could, the simple
relationship

$$P_c = Z_c RT_c / V_c \tag{F-4}$$

could be used to correlate critical pressures.

## F.2 Correlation of Critical Compressibility Factors

A survey of the literature indicated that there were
sufficient experimental data for 27 binary systems to permit

calculation of $Z_c$. There were 8 binary systems containing methane and the experimental data (including $Z_c$ values calculated using Equation F-4) are presented in Table F-1. The experimental data for systems containing ethane and propane are presented in Tables F-2 and F-3, respectively. Table F-4 gives the data for several miscellaneous systems. The data presented in these tables indicates a systematic variation of $Z_c$ values with respect to composition and chemical species.

Since there were experimental data for only a few systems it was important that the correlation procedure could be generalized to systems for which there was no data. Thus, having regard for the work of Chueh and Prausnitz, the relationship

$$Z_c = \sum_i \phi_i Z_{ci} + \sum_i \sum_j \phi_i \phi_j Z_{cij} \qquad (F-5)$$

where:  $Z_{ci}$ is the critical compressibility factor for pure component i,

$Z_{cij}$ is a correlation parameter which characterizes the effects of the i-j interactions on the critical compressibility factor.

was tried with various weightings (mole fraction, weight fraction, diameter fraction, surface fraction and volume fraction). The weight fraction weighting generally gave the best fit of the data to Equation F-5, however, there was some indication that the nature of $Z_c$ behavior is too complex to be approximated by a simple quadratic function such as Equation F-5. The "$Z_c$ excess" defined by

$$Z_c{}' = Z_c - \sum_i \phi_i Z_{ci} \qquad (F-6)$$

are presented in Figure F-1 for the methane binaries. The $Z_{cij}$ parameters are simply one half the $Z_c{}'$ values at the

apex of the parabola. There is an orderly variation with chemical species, but the data for methane-n-butane, methane-n-pentane and methane-n-heptane show considerable scatter with respect to composition as reflected by the weight fraction methane in the mixture. Figure F-2 shows the $Z_{cij}$ correlation parameters to correlate remarkably well with the absolute value of the difference in critical temperatures of the chemical species.

Some caution must be exercised in extending the $Z_c$ correlation over the full range of composition. It is known that the methane-n-heptane and the methane-n-decane systems both exhibit complex liquid-liquid immiscibility and/or formation of solids at low temperatures.

The $Z_c'$ correlations for the ethane and propane binary systems are presented in Figures F-3 and F-4, respectively. There are wide variations from the curves predicted by Equation F-5. It should be appreciated, however, that $Z_c$ values are subject to considerable error since it is extremely difficult to determine critical volumes.

## F.3  Correlation of Critical Pressures

The large discrepancies in the correlation of $Z_c$ values prevented quantitative estimation of critical pressures using Equation F-4. An independent test of the suitability of the general procedure was made by fitting

$$P_c = \frac{(\phi_1 Z_{c1} + \phi_2 Z_{c2} + 2\phi_1\phi_2 Z_{c12}) R(\phi_1 T_{c1} + \phi_2 T_{c2} + 2\phi_1\phi_2 T_{c12})}{\phi_1 V_{c1} + \phi_2 V_{c2} + 2\phi_1\phi_2 V_{c12}}$$

(F-7)

to the data using a least squares criterion to minimize the error in $P_c$. The least squares estimators $T_{c12}$, $V_{c12}$ and $Z_{c12}$ were very much different from the correlation parameters obtained using Equations F-1, F-2 and F-5, respectively. This showed that there are serious deficiencies in both the data and the model.

TABLE F-1.   CRITICAL STATE DATA FOR SOME METHANE BINARIES

CRITICAL STATE DATA FOR METHANE AND PROPANE

AUTHOR(S) - SAGE, B.H., W.N. LACEY, AND J.G. SCHAAFSMA.
REFERENCE - I.E.C., 26, 214, (1934).

---------------------- PURE COMPONENT DATA -----------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 5.960 | 0.013 |
| 0.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |

---------------------- MIXTURE CRITICAL DATA ----------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.1000 | 41.288 | 765.7 | 2.850 | 655.50 | 0.310 | 7.006 | 0.150 |
| 0.2000 | 38.483 | 890.6 | 2.660 | 637.90 | 0.346 | 7.162 | 0.141 |
| 0.3000 | 35.678 | 1018.4 | 2.460 | 619.30 | 0.373 | 7.331 | 0.131 |
| 0.4000 | 32.873 | 1153.0 | 2.280 | 598.40 | 0.411 | 7.752 | 0.120 |
| 0.5000 | 30.069 | 1291.8 | 2.085 | 575.00 | 0.436 | 7.694 | 0.107 |
| 0.6000 | 27.262 | 1406.4 | 1.907 | 547.70 | 0.456 | 7.500 | 0.092 |
| 0.7000 | 24.457 | 1468.1 | 1.740 | 510.40 | 0.446 | 7.512 | 0.075 |

AUTHOR(S) - REAMER, H.H., B.H. SAGE, AND W.N. LACEY.
REFERENCE - I.E.C., 42, 534, (1950).

---------------------- PURE COMPONENT DATA -----------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 5.960 | 0.013 |
| 0.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |

---------------------- MIXTURE CRITICAL DATA ----------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.1400 | 40.208 | 707.0 | 3.240 | 649.69 | 0.356 | 7.489 | 0.147 |
| 0.3228 | 35.038 | 1020.0 | 2.555 | 619.69 | 0.391 | 7.793 | 0.129 |
| 0.4691 | 30.934 | 1218.0 | 2.307 | 589.69 | 0.444 | 7.706 | 0.111 |
| 0.5082 | 27.593 | 1353.0 | 2.083 | 559.69 | 0.489 | 7.616 | 0.094 |

TABLE F-1  (Cont.)

CRITICAL STATE DATA FOR METHANE AND n-BUTANE

AUTHOR(S) - SAGE, BUDD, HICKS AND W. N. LACEY.
REFERENCE - Ind.Eng.Chem., 32: 1085, (1940).

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 16.042 | 669.7 | 1.590 | 343.13 | 0.289 | 5.860 | 0.013 |
| 0.0000 | 58.120 | 551.1 | 4.080 | 765.29 | 0.274 | 6.770 | 0.201 |

MIXTURE CRITICAL DATA

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.3600 | 42.571 | 1254.0 | 2.970 | 709.09 | 0.449 | 8.003 | 0.172 |
| 0.4720 | 38.250 | 1521.0 | 2.657 | 679.67 | 0.491 | 7.928 | 0.156 |
| 0.5500 | 34.977 | 1666.0 | 2.121 | 649.60 | 0.516 | 7.859 | 0.142 |
| 0.6160 | 32.199 | 1768.0 | 1.894 | 619.09 | 0.531 | 7.791 | 0.129 |
| 0.6721 | 29.843 | 1790. | 1.710 | 589.69 | 0.536 | 7.726 | 0.116 |
| 0.7240 | 27.645 | 1812.0 | 1.580 | 559.67 | 0.535 | 7.659 | 0.103 |
| 0.7710 | 25.647 | 1848.0 | 1.494 | 525.69 | 0.539 | 7.590 | 0.090 |

CRITICAL STATE DATA FOR METHANE AND i-PENTANE

AUTHOR(S) - OLDS, REAMER, SAGE, AND W. N. LACEY.
REFERENCE - Ind.Eng.Chem. 34: 1008, (1942).

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 5.860 | 0.013 |
| 0.0000 | 58.120 | 529.1 | 4.210 | 734.63 | 0.283 | 6.540 | 0.187 |

MIXTURE CRITICAL DATA

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.3369 | 43.943 | 1085.0 | 3.150 | 679.69 | 0.432 | 7.943 | 0.163 |
| 0.5075 | 34.651 | 1467.0 | 2.230 | 619.69 | 0.494 | 7.792 | 0.131 |
| 0.5895 | 29.107 | 1679.0 | 1.808 | 559.69 | 0.521 | 7.658 | 0.104 |

TABLE F-1  (Cont.)

CRITICAL STATE DATA FOR METHANE AND N-PENTANE

AUTHOR(S) - SAGE, B.H., H.H. REAMER, R.H. OLDS, AND W.N. LACEY.
REFERENCE - I.E.C., 34, 1108, (1942).

------------------------- PURE COMPONENT DATA -------------------------

| OL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| CH4 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
|-------|---------|------|-------|-------|------|--------|--------|
| 1.0000 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 5.860 | 0.013 |
| 0.0000 | 72.146 | 487.5 | 4.730 | 845.00 | 0.234 | 7.030 | 0.252 |

------------------------- MIXTURE CRITICAL DATA -------------------------

| VOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| CH4 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
|--------|---------|--------|-------|--------|-------|--------|--------|
| 0.2950 | 55.595 | 1625.0 | 3.691 | 799.69 | 0.440 | 8.313 | 0.236 |
| 0.5211 | 42.910 | 1510.0 | 2.820 | 739.69 | 0.572 | 8.139 | 0.1 |
| 0.6705 | 34.528 | 2081.0 | 2.261 | 679.69 | 0.645 | 7.944 | 0.159 |
| 0.7665 | 29.142 | 2338.0 | 1.876 | 619.69 | 0.659 | 7.774 | 0.126 |
| 0.8236 | 25.938 | 2455.0 | 1.652 | 559.69 | 0.634 | 7.651 | 0.102 |

CRITICAL STATE DATA FOR METHANE AND N-HEPTANE

AUTHOR(S) - REAMER, H.H., B.H. SAGE, AND W.N. LACEY.
REFERENCE - J. CHEM. ENG. DATA, 1, 29, (1956).

------------------------- PURE COMPONENT DATA -------------------------

| OL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| CH4 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
|-------|---------|------|-------|-------|------|--------|--------|
| 1.0000 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 5.860 | 0.013 |
| 0.0000 | 100.198 | 397.5 | 6.920 | 972.25 | 0.264 | 7.370 | 0.352 |

------------------------- MIXTURE CRITICAL DATA -------------------------

| VOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| CH4 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
|--------|---------|--------|-------|--------|-------|--------|--------|
| 0.4410 | 63.035 | 1206.0 | 4.500 | 919.69 | 0.549 | 8.732 | 0.320 |
| 0.5850 | 50.966 | 1906.0 | 3.300 | 859.69 | 0.681 | 8.559 | 0.279 |
| 0.6720 | 43.645 | 2469.0 | 2.485 | 799.69 | 0.715 | 8.386 | 0.243 |
| 0.7320 | 38.595 | 2927.0 | 2.091 | 739.69 | 0.771 | 8.236 | 0.214 |
| 0.7780 | 34.724 | 3298.0 | 1.766 | 679.69 | 0.798 | 8.102 | 0.187 |
| 0.8170 | 31.442 | 3549.0 | 1.501 | 619.69 | 0.801 | 7.974 | 0.163 |
| 0.8550 | 28.244 | 3609.0 | 1.215 | 559.69 | 0.790 | 7.934 | 0.136 |
| 0.8940 | 24.930 | 3520.0 | 1.112 | 499.69 | 0.783 | 7.810 | 0.105 |

TABLE F-1   (Cont.)

CRITICAL STATE DATA FOR METHANE AND N-OCTANE

AUTHOR(S) - SHIPMAN, L... AND J.P. KOHN.
REFERENCE - J. CHEM. ENG. DATA, 11, 176, (1966).

---------------------------- PURE COMPONENT DATA ----------------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 16.042 | 669.7 | 1.590 | 343.13 | 0.288 | 5.860 | 0.013 |
| 0.0000 | 128.250 | 332.0 | 6.750 | 1070.01 | 0.254 | 7.940 | 0.430 |

---------------------------- MIXTURE CRITICAL DATA ----------------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.8600 | 31.751 | 4600.0 | 1.410 | 620.69 | 0.964 | 8.070 | 0.180 |
| 0.8720 | 30.404 | 4673.0 | 1.270 | 581.69 | 0.950 | 8.005 | 0.167 |
| 0.8900 | 29.606 | 4684.0 | 1.176 | 536.69 | 0.957 | 7.960 | 0.159 |
| 0.8950 | 28.945 | 4673.0 | 1.100 | 491.69 | 0.974 | 7.931 | 0.153 |

CRITICAL STATE DATA FOR METHANE AND N-DECANE

AUTHOR(S) - REAMER, H.H., R.H. OLDS, B.H. SAGE, AND W.N. LACEY.
REFERENCE - I.E.C., 34, 1526, (1942).

---------------------------- PURE COMPONENT DATA ----------------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 16.042 | 669.7 | 1.590 | 342.13 | 0.288 | 5.860 | 0.013 |
| 0.0000 | 142.276 | 304.0 | 9.660 | 1111.70 | 0.246 | 8.180 | 0.466 |

---------------------------- MIXTURE CRITICAL DATA ----------------------------

| MOL FR CH4 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.7389 | 49.001 | 2911.0 | 2.954 | 919.69 | 0.871 | 8.611 | 0.322 |
| 0.7979 | 41.553 | 3605.0 | 2.377 | 859.69 | 0.928 | 8.539 | 0.269 |
| 0.8333 | 37.085 | 4163.0 | 1.983 | 799.69 | 0.964 | 8.353 | 0.233 |
| 0.8574 | 34.042 | 4580.0 | 1.716 | 739.69 | 0.990 | 8.210 | 0.206 |
| 0.8767 | 31.606 | 4935.0 | 1.495 | 679.69 | 1.011 | 8.091 | 0.183 |
| 0.8912 | 29.776 | 5180.0 | 1.322 | 619.69 | 1.029 | 7.996 | 0.165 |
| 0.8979 | 28.930 | 5310.0 | 1.180 | 559.69 | 1.043 | 7.951 | 0.157 |

TABLE F-1  (Cont.)

CRITICAL STATE DATA FOR ETHANE AND HYDROGEN SULFIDE

AUTHOR(S) - REAMER, H.H., B.H. SAGE AND W.N. LACEY.
REFERENCE - I.E.C., 43, 976, (1951).

| ---------------------------- PURE COMPONENT DATA ---------------------------- | | | | | | | |
| MOL FR | MOLE WT | PC | VC | TC | ZC | MODFL PITZER | |
| CH4 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 1.0000 | 16.042 | 667.7 | 1.590 | 343.13 | 0.288 | 5.460 | 0.013 |
| 0.0000 | 34.076 | 1306.0 | 1.570 | 672.40 | 0.283 | 6.000 | 0.100 |

| ---------------------------- MIXTURE CRITICAL DATA ---------------------------- | | | | | | | |
| MOL FR | MOLE WT | PC | VC | TC | ZC | MODEL PITZER | |
| CH4 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 0.2000 | 30.516 | 1600.0 | 1.293 | 519.00 | 0.322 | 7.031 | 0.087 |
| 0.3500 | 27.078 | 1907.0 | 1.134 | 559.00 | 0.375 | 7.097 | 0.072 |
| 0.5500 | 24.157 | 1947.0 | 1.093 | 497.69 | 0.397 | 7.366 | 0.055 |

# TABLE F-2.   CRITICAL STATE DATA FOR SOME ETHANE BINARIES

CRITICAL STATE DATA FOR ETHANE AND PENTANE

AUTHOR(S) — KAY, W.B.
REFERENCE — I.E.C., 32, 353, (1940).

| MOL FR C2H6 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 30.068 | 708.0 | 2.370 | 549.77 | 0.285 | 6.260 | 0.105 |
| 0.0000 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 6.770 | 0.201 |

MIXTURE CRITICAL DATA

| MOL FR C2H6 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.1749 | 53.213 | 546.1 | 3.631 | 742.79 | 0.290 | 6.321 | 0.196 |
| 0.4510 | 45.403 | 730.7 | 3.025 | 697.27 | 0.315 | 8.007 | 0.170 |
| 0.6577 | 39.070 | 841.6 | 2.600 | 650.61 | 0.313 | 7.633 | 0.161 |
| 0.8219 | 35.068 | 837.2 | 2.450 | 607.17 | 0.313 | 7.420 | 0.129 |
| 0.9472 | 31.549 | 756.2 | 2.345 | 568.09 | 0.279 | 7.425 | 0.105 |


CRITICAL STATE DATA FOR ETHANE AND N-PENTANE

AUTHOR(S) — REAMER, H.H., B.H. SAGE, AND W.N. LACEY.
REFERENCE — J. CHEM. ENG. DATA, 5, 44, (1960).

| MOL FR C2H6 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 30.068 | 708.3 | 2.370 | 549.77 | 0.295 | 6.280 | 0.105 |
| 0.0000 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 7.030 | 0.252 |

MIXTURE CRITICAL DATA

| MOL FR C2H6 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.2946 | 59.764 | 741.5 | 3.720 | 799.69 | 0.324 | 8.382 | 0.237 |
| 0.5630 | 48.436 | 953.5 | 2.805 | 759.62 | 0.344 | 8.177 | 0.201 |
| 0.7189 | 41.595 | 980.0 | 2.405 | 678.69 | 0.326 | 8.039 | 0.171 |
| 0.8502 | 36.371 | 923.5 | 2.185 | 619.69 | 0.303 | 7.894 | 0.141 |
| 0.9779 | 31.052 | 796.0 | 2.235 | 559.69 | 0.281 | 7.723 | 0.107 |

TABLE F-2  (Cont.)

CRITICAL STATE DATA FOR ETHANE AND N-HEPTANE

AUTHOR(S) - KAY, W.B.
REFERENCE - IND.ENG. 30, 459, (1938).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ----- | ----- | ----- | PURE COMPONENT DATA | ----- | ----- | ----- | ----- |
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| C2H6 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| 1.0000 | 30.068 | 708.3 | 2.370 | 549.77 | 0.285 | 6.290 | 0.105 |
| 0.0000 | 100.198 | 397.0 | 6.920 | 972.25 | 0.254 | 7.570 | 0.352 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ----- | ----- | ----- | MIXTURE CRITICAL DATA | ----- | ----- | ----- | ----- |
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| C2H6 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| 0.2554 | 81.500 | 687.0 | 5.025 | 927.09 | 0.344 | 8.327 | 0.369 |
| 0.5871 | 59.024 | 11.00 | 3.150 | 833.09 | 0.438 | 8.350 | 0.273 |
| 0.7709 | 48.184 | 1203.0 | 2.65 | 736.09 | 0.423 | 8.243 | 0.210 |
| 0.8771 | 37.015 | 1152.0 | 2.240 | 649.49 | 0.383 | 7.955 | 0.159 |
| 0.9583 | 32.201 | 950.0 | 2.086 | 579.09 | 0.204 | 7.777 | 0.118 |

CRITICAL STATE DATA FOR ETHANE AND N-DECANE

AUTHOR(S) - REAMER, H.H., AND B.H. SAGE.
REFERENCE - J. CHEM. ENG. DATA, 7, 161, (1962).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ----- | ----- | ----- | PURE COMPONENT DATA | ----- | ----- | ----- | ----- |
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| C2H6 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| 1.0000 | 30.068 | 708.3 | 2.370 | 549.77 | 0.285 | 6.290 | 0.105 |
| 0.0000 | 142.276 | 304.0 | 9.660 | 1111.70 | 0.246 | 8.180 | 0.485 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ----- | ----- | ----- | MIXTURE CRITICAL DATA | ----- | ----- | ----- | ----- |
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| C2H6 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| 0.6980 | 63.954 | 1491.0 | 3.916 | 919.69 | 0.587 | 8.877 | 0.232 |
| 0.7780 | 54.978 | 1540.0 | 3.249 | 859.69 | 0.577 | 8.622 | 0.291 |
| 0.8350 | 48.982 | 1710.0 | 2.787 | 799.69 | 0.556 | 8.416 | 0.241 |
| 0.8890 | 42.035 | 1687.0 | 2.407 | 739.69 | 0.511 | 8.204 | 0.199 |
| 0.9270 | 38.259 | 1510.0 | 2.022 | 679.69 | 0.421 | 8.035 | 0.167 |
| 0.9640 | 34.107 | 1184.0 | 1.756 | 619.69 | 0.314 | 7.865 | 0.134 |
| 0.9950 | 30.629 | 778.0 | 2.142 | 559.69 | 0.277 | 7.715 | 0.105 |

TABLE F-2   (Cont.)

CRITICAL STATE DATA

AUTHOR(S) — KAY,

REFERENCE — I. E. C.,

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| C2H6 | MOLE WT LB/MOLE | PC PSIA | VC FT3/ | TC DEG R | ZC | ACENT ALPHA | PITZER OMEGA |
|------|------|------|------|------|------|------|------|
| 1. | 30.0 | 7 | 2. | 549.7 | 0.28 | 6. | .10 |
| 0. | 34.07 | 13 | 1. | 672.4 | 0.28 | 6. | .10 |

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PSEUDO CRITICAL DATA

| C2H6 | MOLE WT LB/MOLE | PC PSIA | VC FT3/ | TC DEG R | ZC | ACENT ALPHA | PITZER OMEGA |
|------|------|------|------|------|------|------|------|
| 0.1 | 3 .6 | 121 . | 1.45 | 64 .73 | 0.284 | 7. | . |
| 0.29 | 32.91 | 10 .4 | 1.5 | 14.6 | 0.27 | 7.0 | . |
| 0.4 | 32.0 | 91 . | 1. | . 20 | 0.2 | 7. | . |
| 0.5 | 31. | 8 1.1 | 2.0 | 6 .34 | 0.7 | 7. 1 | . 9 |
| 0.7 | 3. | 7 . | 2.21 | .7. 9 | . | 7. | . |
| 0.9 | 3 . | 7 . | 2.0 | . 1. 4 | 0.28 | . | . |

TABLE F-3.   CRITICAL STATE DATA FOR SOME PROPANE BINARIES

CRITICAL STATE DATA FOR PROPANE AND N-BUTANE

AUTHOR(S) - NYSEWANDER, C.H., B.H. SAGE, AND W.N. LACEY.
REFERENCE - I.E.C., 32, 118, (1940).

------------------------- PURE COMPONENT DATA -------------------------

| MOL FR C3H8 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |
| 0.0000 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 6.770 | 0.201 |

------------------------- MIXTURE CRITICAL DATA -------------------------

| MOL FR C3H8 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.2030 | 55.272 | 598.0 | 3.920 | 750.09 | 0.286 | 8.125 | 0.198 |
| 0.3390 | 53.365 | 609.0 | 3.840 | 739.89 | 0.294 | 8.101 | 0.192 |
| 0.5160 | 50.882 | 630.0 | 3.660 | 724.09 | 0.296 | 8.065 | 0.184 |
| 0.6950 | 48.371 | 638.0 | 3.430 | 703.19 | 0.289 | 8.025 | 0.175 |
| 0.8550 | 46.127 | 631.0 | 3.270 | 684.09 | 0.281 | 7.985 | 0.166 |

CRITICAL STATE DATA FOR PROPANE AND N-PENTANE

AUTHOR(S) - SAGE, B.H., B.L. HICKS, AND W.N. LACEY.
REFERENCE - I.E.C., 32, 992, (1940).

------------------------- PURE COMPONENT DATA -------------------------

| MOL FR C3H8 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |
| 0.0000 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 7.030 | 0.252 |

------------------------- MIXTURE CRITICAL DATA -------------------------

| MOL FR C3H8 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.3498 | 62.333 | 608.0 | 4.360 | 798.69 | 0.309 | 8.291 | 0.233 |
| 0.5557 | 56.557 | 648.0 | 3.960 | 760.59 | 0.314 | 8.207 | 0.213 |
| 0.7921 | 49.926 | 671.0 | 3.440 | 715.49 | 0.300 | 8.081 | 0.196 |
| 0.8190 | 49.171 | 664.0 | 3.390 | 710.09 | 0.295 | 8.065 | 0.183 |

TABLE F-3   (Cont.)

CRITICAL STATE DATA FOR PROPANE AND I-PENTANE

AUTHOR(S) - VAUGHN, W.E., AND F.C. COLLINS.
REFERENCE - I.E.C., 34, 885, (1942).

------------------------- PURE COMPONENT DATA -------------------------

| MOL FR<br>C3H8 | MOLE WT<br>LB/MOLE | PC<br>PSIA | VC<br>FT**3 | TC<br>DEG R | ZC | RIEDEL<br>ALPHA | PITZER<br>OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |
| 0.0000 | 72.146 | 494.7 | 4.900 | 828.70 | 0.273 | 6.870 | 0.215 |

------------------------- MIXTURE CRITICAL DATA -------------------------

| MOL FR<br>C3H8 | MOLE WT<br>LB/MOLE | PC<br>PSIA | VC<br>FT**3 | TC<br>DEG R | ZC | RIEDEL<br>ALPHA | PITZER<br>OMEGA |
|---|---|---|---|---|---|---|---|
| 0.1010 | 69.312 | 520.3 | 4.500 | 817.67 | 0.279 | 8.261 | 0.231 |
| 0.3930 | 61.121 | 614.0 | 3.780 | 780.00 | 0.277 | 8.197 | 0.214 |
| 0.5880 | 55.651 | 652.4 | 3.460 | 748.00 | 0.281 | 8.134 | 0.199 |
| 0.7940 | 49.872 | 652.8 | 3.220 | 710.20 | 0.280 | 8.049 | 0.180 |
| 0.8990 | 46.927 | 648.8 | 3.160 | 688.40 | 0.277 | 7.999 | 0.169 |

CRITICAL STATE DATA FOR PROPANE AND N-DECANE

AUTHOR(S) - REAMER, H.H., AND B.H. SAGE.
REFERENCE - J. CHEM. ENG. DATA, 11, 17, (1966).

------------------------- PURE COMPONENT DATA -------------------------

| MOL FR<br>C3H8 | MOLE WT<br>LB/MOLE | PC<br>PSIA | VC<br>FT**3 | TC<br>DEG R | ZC | RIEDEL<br>ALPHA | PITZER<br>OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |
| 0.0000 | 142.276 | 304.0 | 9.660 | 1111.70 | 0.246 | 8.180 | 0.466 |

------------------------- MIXTURE CRITICAL DATA -------------------------

| MOL FR<br>C3H8 | MOLE WT<br>LB/MOLE | PC<br>PSIA | VC<br>FT**3 | TC<br>DEG R | ZC | RIEDEL<br>ALPHA | PITZER<br>OMEGA |
|---|---|---|---|---|---|---|---|
| 0.7120 | 72.370 | 988.0 | 4.500 | 919.69 | 0.450 | 8.768 | 0.321 |
| 0.7993 | 63.799 | 1028.0 | 3.780 | 859.69 | 0.421 | 8.552 | 0.277 |
| 0.8673 | 57.122 | 980.0 | 3.270 | 799.69 | 0.373 | 8.363 | 0.240 |
| 0.9283 | 51.133 | 873.0 | 3.220 | 739.69 | 0.354 | 8.180 | 0.204 |
| 0.9870 | 45.370 | 678.0 | 3.210 | 679.69 | 0.298 | 7.989 | 0.166 |

TABLE F-3 (Cont.)

CRITICAL STATE DATA FOR HYDROGEN SULFIDE AND PROPANE

AUTHOR(S) - KAY, W.B., AND G. M. RAMBOSEK.
REFERENCE - I.E.C., 45, 221, (1953).

| | | | PURE COMPONENT DATA | | | | |
|---|---|---|---|---|---|---|---|
| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
| 1.0000 | 34.076 | 1306.0 | 1.570 | 672.40 | 0.283 | 6.800 | 0.100 |
| 0.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |

| | | | MIXTURE CRITICAL DATA | | | | |
|---|---|---|---|---|---|---|---|
| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
| 0.1633 | 42.458 | 695.0 | 2.979 | 657.24 | 0.283 | 8.051 | 0.164 |
| 0.2986 | 41.192 | 759.2 | 2.878 | 651.04 | 0.291 | 8.095 | 0.163 |
| 0.4342 | 39.744 | 821.7 | 2.450 | 648.02 | 0.295 | 8.110 | 0.157 |
| 0.5641 | 38.442 | 887.6 | 2.261 | 643.98 | 0.292 | 8.102 | 0.148 |
| 0.6755 | 37.326 | 956.0 | 2.097 | 644.90 | 0.289 | 8.090 | 0.139 |
| 0.7817 | 36.262 | 1043.2 | 1.914 | 648.13 | 0.285 | 8.008 | 0.129 |
| 0.8984 | 35.093 | 1150.0 | 1.720 | 655.63 | 0.282 | 8.016 | 0.117 |

CRITICAL STATE DATA FOR CARBON DIOXIDE AND PROPANE

AUTHOR(S) - REAMER, H.H., B.H. SAGE, AND W.N. LACEY.
REFERENCE - I.E.C., 43, 2515, (1951).

| | | | PURE COMPONENT DATA | | | | |
|---|---|---|---|---|---|---|---|
| MOL FR CO2 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
| 1.0000 | 44.010 | 1070.6 | 1.510 | 547.49 | 0.275 | 6.900 | 0.225 |
| 0.0000 | 44.094 | 616.3 | 3.210 | 665.68 | 0.276 | 6.540 | 0.152 |

| | | | MIXTURE CRITICAL DATA | | | | |
|---|---|---|---|---|---|---|---|
| MOL FR CO2 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
| 0.4070 | 44.059 | 970.0 | 2.270 | 619.61 | 0.333 | 8.089 | 0.269 |
| 0.6090 | 44.051 | 992.0 | 2.070 | 549.00 | 0.324 | 8.220 | 0.294 |
| 0.7950 | 44.027 | 1010.0 | 1.700 | 559.89 | 0.285 | 9.287 | 0.367 |

TABLE F-4.   CRITICAL STATE DATA FOR SOME MISCELLANEOUS BINARIES

CRITICAL STATE DATA FOR N-BUTANE AND N-HEPTANE

AUTHOR(S) - KAY, W.B.
REFERENCE - I.E.C., 33, 590, (1941).

----------------------------- PURE COMPONENT DATA -----------------------------

| MOL FR C4H10 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 6.770 | 0.201 |
| 0.0000 | 100.198 | 397.5 | 6.920 | 972.25 | 0.264 | 7.570 | 0.352 |

----------------------------- MIXTURE CRITICAL DATA -----------------------------

| MOL FR C4H10 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.1590 | 93.507 | 451.6 | 5.960 | 951.82 | 0.263 | 8.768 | 0.339 |
| 0.4249 | 82.319 | 538.0 | 5.050 | 908.62 | 0.278 | 8.638 | 0.308 |
| 0.6311 | 73.642 | 584.4 | 4.530 | 867.33 | 0.284 | 8.496 | 0.276 |
| 0.8010 | 66.493 | 596.1 | 4.220 | 825.86 | 0.283 | 8.353 | 0.246 |
| 0.9401 | 60.640 | 575.3 | 4.060 | 785.20 | 0.277 | 8.219 | 0.218 |

CRITICAL STATE DATA FOR N-BUTANE AND N-DECANE

AUTHOR(S) - REAMER, H.H., AND B.H. SAGE.
REFERENCE - J. CHEM. ENG. DATA, 9, 24, (1964).

----------------------------- PURE COMPONENT DATA -----------------------------

| MOL FR C4H10 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 6.770 | 0.201 |
| 0.0000 | 142.276 | 304.0 | 9.660 | 1111.70 | 0.246 | 8.180 | 0.466 |

----------------------------- MIXTURE CRITICAL DATA -----------------------------

| MOL FR C4H10 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.7390 | 80.034 | 714.0 | 4.970 | 919.69 | 0.359 | 8.719 | 0.318 |
| 0.8650 | 69.481 | 694.2 | 4.220 | 859.69 | 0.317 | 8.466 | 0.267 |
| 0.9560 | 61.822 | 616.3 | 4.000 | 799.69 | 0.287 | 8.262 | 0.226 |

TABLE F-4 (Cont.)

CRITICAL STATE DATA FOR CARBON DIOXIDE AND N-BUTANE

AUTHOR(S) - OLDS, R. H., H. H. REAMER, B. H. SAGE, AND W. N. LACEY.
REFERENCE - I.E.C., 41, 475, (1949).

------------------------- PURE COMPONENT DATA -------------------------
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| CO2 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 1.00000 | 44.011 | 1073.6 | 1.511 | 547.47 | 0.275 | 6.520 | 0.225 |
| 0.00000 | 58.120 | 550.7 | 4.080 | 765.29 | 0.274 | 6.770 | 0.201 |

------------------------- MIXTURE CRITICAL DATA -------------------------
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| CO2 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 0.1787 | 53.600 | 741.0 | 3.490 | 742.09 | 0.323 | 8.491 | 0.255 |
| 0.3240 | 50.020 | 912.0 | 3.010 | 717.79 | 0.305 | 8.780 | 0.213 |
| 0.5016 | 51.040 | 1100.0 | 2.400 | 678.99 | 0.390 | 9.012 | 0.391 |
| 0.6016 | 41.710 | 1145.0 | 2.110 | 633.09 | 0.389 | 9.230 | 0.153 |
| 0.8510 | 46.410 | 1147.0 | 1.910 | 566.09 | 0.306 | 9.420 | 0.342 |

CRITICAL STATE DATA FOR N-PENTANE AND N-HEPTANE

AUTHOR(S) - CUMMINGS, L. W. T., F. W. STONE, AND M. A. VOLANTE.
REFERENCE - I.E.C., 25, 720, (1933).

------------------------- PURE COMPONENT DATA -------------------------
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| C5H12 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 1.0000 | 72.146 | 487.3 | 4.730 | 845.06 | 0.264 | 7.030 | 0.252 |
| 0.0000 | 100.198 | 397.8 | 6.920 | 972.25 | 0.264 | 7.570 | 0.302 |

------------------------- MIXTURE CRITICAL DATA -------------------------
| MOL FR | MOLE WT | PC | VC | TC | ZC | RIEDEL | PITZER |
| C5H12 | LB/MOLE | PSIA | FT**3 | DEG R | | ALPHA | OMEGA |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 0.2950 | 93.044 | 434.5 | 5.960 | 948.00 | 0.254 | 8.736 | 0.333 |
| 0.5580 | 84.540 | 479.1 | 5.080 | 911.00 | 0.248 | 8.614 | 0.306 |
| 0.7470 | 79.243 | 492.3 | 4.820 | 847.70 | 0.249 | 8.524 | 0.286 |

TABLE F-4  (Cont.)

CRITICAL STATE DATA FOR HYDROGEN SULFIDE AND CARBON DIOXIDE

AUTHOR(S) — BIERLEIN, J.A., AND W.B. KAY.
REFERENCE — I.E.C., 45, 618, (1953).

--------------------------------- PURE COMPONENT DATA ---------------------------------

| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 34.076 | 1306.0 | 1.570 | 672.40 | 0.283 | 6.250 | 0.100 |
| 0.0000 | 44.010 | 1070.6 | 1.510 | 547.49 | 0.275 | 6.920 | 0.225 |

--------------------------------- MIXTURE CRITICAL DATA ---------------------------------

| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.0991 | 43.025 | 1075.3 | 1.503 | 552.04 | 0.272 | 9.381 | 0.375 |
| 0.1708 | 42.313 | 1085.0 | 1.498 | 556.42 | 0.272 | 9.228 | 0.346 |
| 0.3341 | 40.691 | 1128.8 | 1.491 | 570.39 | 0.274 | 8.914 | 0.286 |
| 0.5272 | 38.772 | 1206.5 | 1.490 | 594.25 | 0.281 | 8.593 | 0.224 |
| 0.6241 | 37.910 | 1245.0 | 1.491 | 608.22 | 0.284 | 8.449 | 0.187 |
| 0.7392 | 36.656 | 1283.5 | 1.499 | 625.75 | 0.286 | 8.290 | 0.160 |
| 0.8386 | 35.679 | 1301.7 | 1.509 | 643.18 | 0.284 | 8.164 | 0.142 |
| 0.9370 | 34.701 | 1304.5 | 1.529 | 659.99 | 0.281 | 8.047 | 0.119 |

CRITICAL STATE DATA FOR HYDROGEN SULFIDE AND N-PENTANE

AUTHOR(S) — REAMER, H.H., B.H. SAGE, AND W.N. LACEY.
REFERENCE — I.E.C., 45, 1805, (1953).

--------------------------------- PURE COMPONENT DATA ---------------------------------

| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 34.076 | 1306.0 | 1.570 | 672.40 | 0.283 | 6.250 | 0.100 |
| 0.0000 | 72.146 | 487.3 | 4.730 | 845.08 | 0.254 | 7.030 | 0.252 |

--------------------------------- MIXTURE CRITICAL DATA ---------------------------------

| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.5960 | 51.740 | 1126.0 | 3.000 | 769.09 | 0.391 | 8.054 | 0.237 |
| 0.7200 | 44.967 | 1245.0 | 2.300 | 739.09 | 0.380 | 8.270 | 0.161 |
| 0.9560 | 35.370 | 1308.0 | 1.640 | 679.00 | 0.292 | 8.033 | 0.117 |

TABLE F-4  (Cont.)

CRITICAL STATE DATA FOR HYDROGEN SULFIDE AND N-DECANE

AUTHOR(S) = REAMER, H.H., P.H. SAGE, AND W. N. LACEY.
REFERENCE = I.E.C., 45, P, (1953).

--------------------------- PURE COMPONENT DATA ---------------------------

| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 34.076 | 1306.0 | 1.570 | 672.40 | 0.283 | 6.250 | 0.100 |
| 0.0000 | 142.276 | 304.00 | 9.660 | 1111.70 | 0.246 | 8.180 | 0.466 |

--------------------------- MIXTURE CRITICAL DATA ---------------------------

| MOL FR H2S | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.9000 | 44.093 | 1935.0 | 1.790 | 700.69 | 0.403 | 8.453 | 0.198 |
| 0.8490 | 39.504 | 1696.0 | 1.480 | 729.69 | 0.309 | 8.225 | 0.134 |
| 0.6940 | 34.729 | 1349.0 | 1.130 | 679.69 | 0.208 | 8.006 | 0.111 |

CRITICAL STATE DATA FOR CARBON DIOXIDE AND N-DECANE

AUTHOR(S) = REAMER, H.H., AND B.H. SAGE.
REFERENCE = J. CHEM. ENG. DATA, 8, 508, (1963).

--------------------------- PURE COMPONENT DATA ---------------------------

| MOL FR CO2 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 1.0000 | 44.010 | 1070.0 | 1.510 | 547.49 | 0.275 | 6.900 | 0.225 |
| 0.0000 | 142.276 | 304.00 | 9.660 | 1111.70 | 0.246 | 8.180 | 0.466 |

--------------------------- MIXTURE CRITICAL DATA ---------------------------

| MOL FR CO2 | MOLE WT LB/MOLE | PC PSIA | VC FT**3 | TC DEG R | ZC | RIEDEL ALPHA | PITZER OMEGA |
|---|---|---|---|---|---|---|---|
| 0.7281 | 70.738 | 3324.0 | 3.170 | 819.69 | 0.714 | 10.412 | 0.543 |
| 0.8030 | 63.171 | 2070.0 | 2.544 | 859.69 | 0.713 | 10.247 | 0.548 |
| 0.8430 | 59.437 | 2720.0 | 2.130 | 789.69 | 0.680 | 10.140 | 0.537 |
| 0.8705 | 56.73 | 2470.0 | 1.861 | 729.69 | 0.632 | 10.000 | 0.512 |
| 0.9046 | 53.31 | 2190.0 | 1.680 | 679.69 | 0.552 | 9.003 | 0.485 |
| 0.9477 | 48.01 | 1600.0 | 1.537 | 619.69 | 0.429 | 9.813 | 0.459 |
| 0.9946 | 44.54 | 1105.0 | 1.500 | 560.69 | 0.290 | 9.631 | 0.423 |
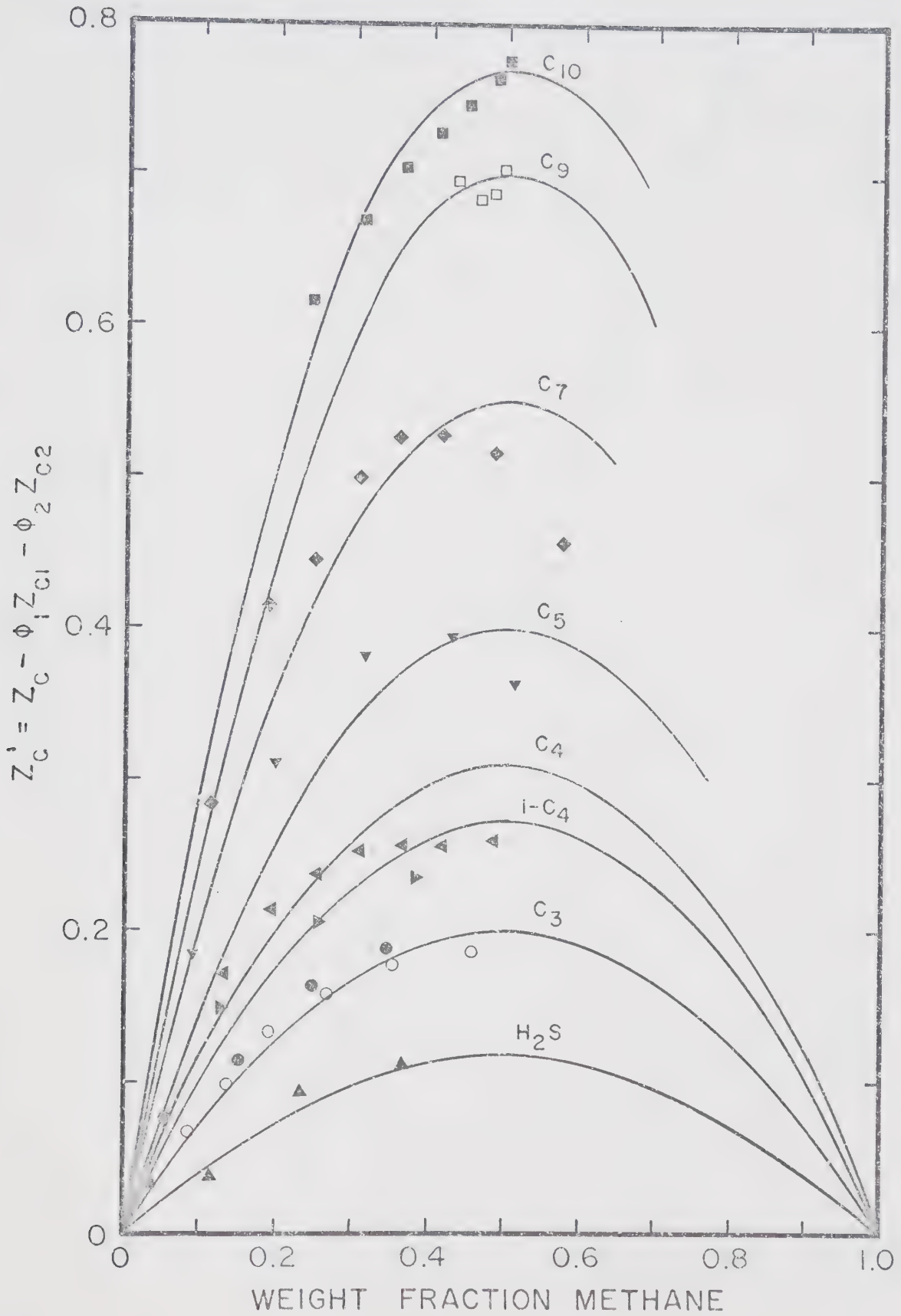
Figure F-1.   $Z_C$ Excess Values for Binary Mixtures Containing Methane.
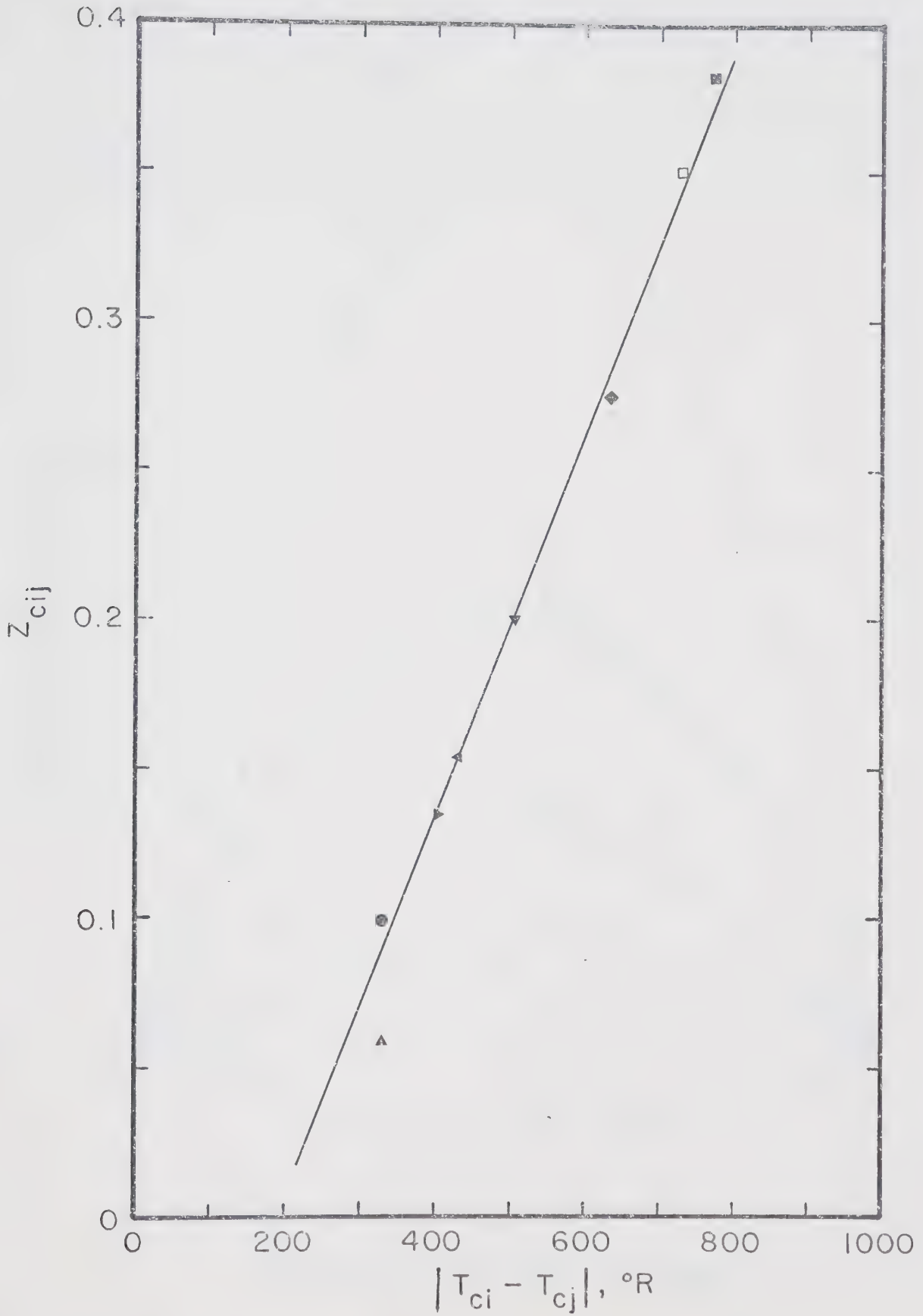
Figure F-2.   Correlation of $Z_{cij}$ with $\left| T_{ci} - T_{cj} \right|$ for Binary
Mixtures Containing Methane.
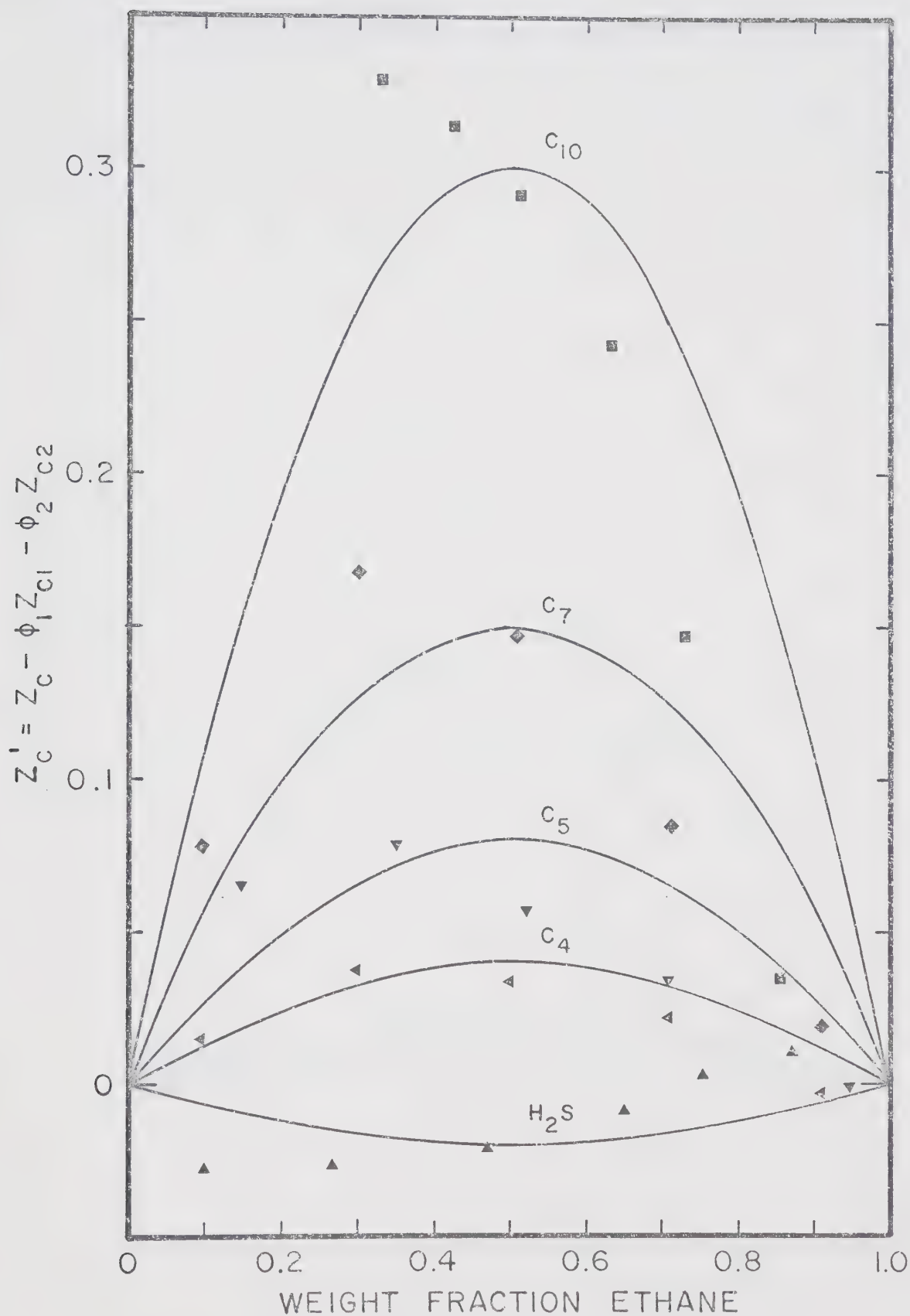
Figure F-3. $Z_c$ Excess Values for Binary Mixtures Containing Ethane.
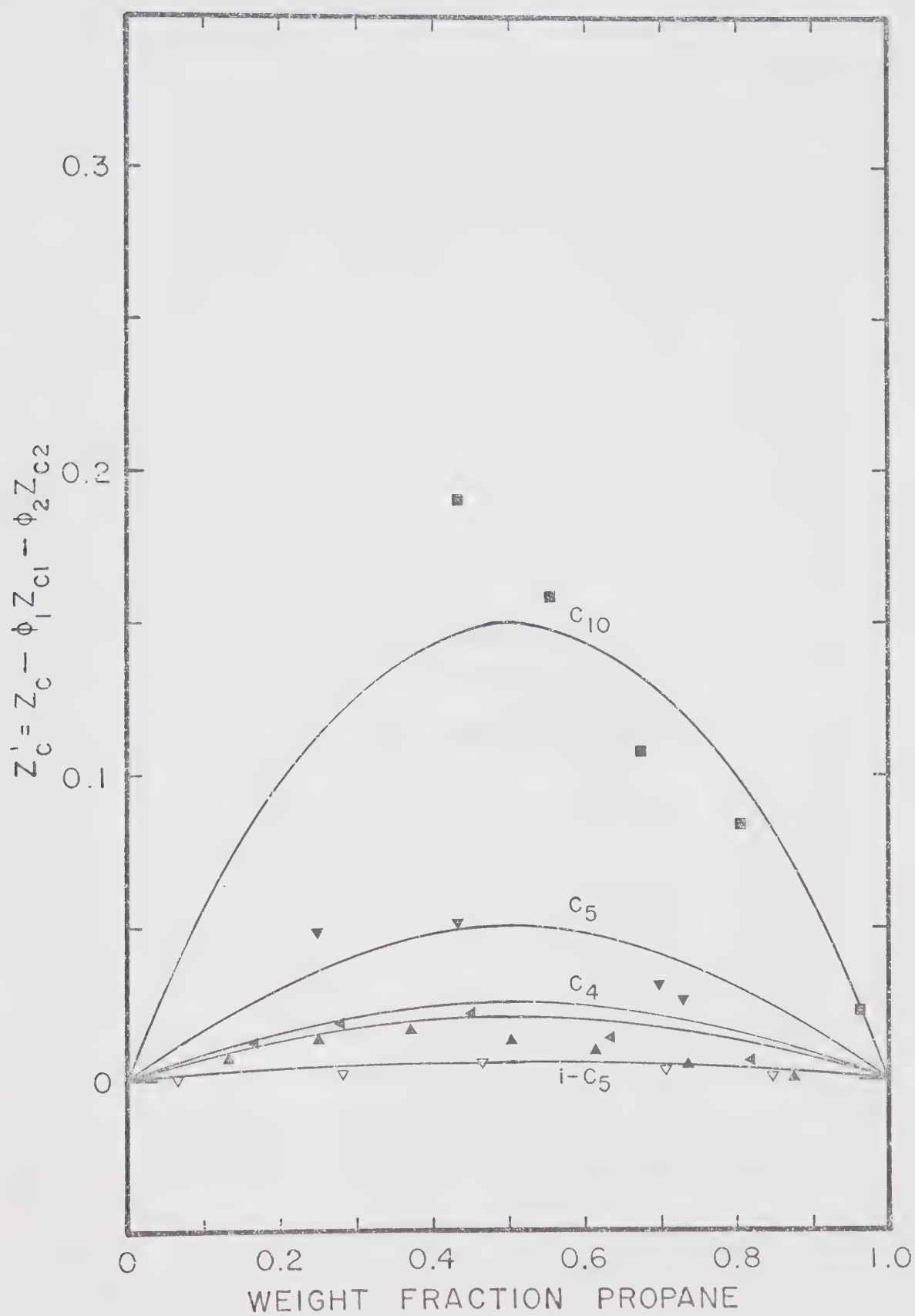
Figure F-4.  $Z_c$ Excess Values for Binary Mixtures Containing Propane.

APPENDIX G

DENSITY BALANCE CALIBRATION

AND DATA REDUCTION PROGRAM

## G.1 Foreword

Vapor phase samples were analyzed with an electro-magnetic gas density balance (R. Fuess Model 184). The density balance was calibrated using gases of known molecular weight. The calibrations were equivalent to preparing a plot of gas density versus the current required to balance the quartz bulb in the balance. The calibration was always made to pass through the origin (i.e. zero current in a high vacuum) by adjusting a small permanent magnet on the balance. Thus, the calibration could be expressed by a single constant representing the slope of the density versus current plot.

The composition of a binary mixture can be calculated from the relationship

$$x_1 = (M_m - M_2)/(M_1 - M_2) \tag{G-1}$$

where: $M_m$ is the molecular weight of the mixture,
$M_1$ is the molecular weight of pure component 1,
$M_2$ is the molecular weight of pure component 2.

The molecular weight of the mixture was calculated from the equation

$$M_m = \rho ZRT/P \tag{G-2}$$

where: $\rho$ is the calculated density using the calibration constant and the current reading,
Z is the compressibility factor of the mixture,
R is the universal gas constant,
T is the absolute temperature of the gas sample in the density balance,
P is the absolute pressure in the density balance based on the manometer reading.

## G.2 Density Balance Calibration

The errors connected with the calibration of the balance

are either random or systematic. It was assumed that the errors in reading currents, pressures and temperatures were random and that by making several measurements they would tend to average out. Impurities in the calibration gases were assumed to cause systematic errors so various calibration gases were used.

The computer print out for two example calibrations using helium are presented in Table G-1. The helium was initially assumed to be pure so a molecular weight of 4.003 was used. The pressure column gives the balance pressures corrected to 0°C. The Z factors were estimated from data on second virial coefficients. The columns "current diff" and "density diff" give the discrepancies between the least squares straight line and the measured currents and the calculated gas densities, respectively. The slope of the calibration line is presented along with the r.m.s. errors in current and density. The first calibration gave a slope of 6.906 gm/m$^3$/ma with a r.m.s. error of 0.0062 ma and 0.043 gm/m$^3$. Tables G-2 and G-3 are calibrations using methane and nitrogen. The calibrations in Table G-4 were made with ultra high purity gases. The calibration constants for methane and carbon dioxide were 6.97 and 6.98, respectively. A value of 6.98 was used in all calculations in this thesis.

In order for the calibration presented in Table G-1 to give the same result the molecular weight of the gas must have been approximately 4.05. A mass spectrometer analysis of the helium used indicated the presence of some nitrogen. A nitrogen content of some 0.17 per cent would give the

# TABLE G-1.  DENSITY BALANCE CALIBRATIONS USING HELIUM

DATA REDUCTION FOR BALANCE CALIBRATION WITH HELIUM
JUNE 25, 1969

DENSITY BALANCE CALIBRATION
GAS MOLE WT =  4.003  SCALE CORR = 0.00

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|----------|--------|---------|---------|----------|----------|
| 1 | 0.6017 | 1.0002 | 14.39 | -0.002 | 99.397 | 0.0198 |
| 2 | 0.5401 | 1.0002 | 12.92 | 0.001 | 89.217 | -0.0082 |
| 3 | 0.4869 | 1.0002 | 11.65 | 0.003 | 80.429 | -0.0255 |
| 4 | 0.4320 | 1.0002 | 10.33 | -0.002 | 71.359 | 0.0205 |
| 5 | 0.3774 | 1.0001 | 9.03 | 0.003 | 62.333 | -0.0274 |
| 6 | 0.3252 | 1.0001 | 7.78 | 0.003 | 53.705 | -0.0229 |
| 7 | 0.2678 | 1.0001 | 6.40 | -0.004 | 44.227 | 0.0289 |
| 8 | 0.1993 | 1.0000 | 4.77 | 0.002 | 32.924 | -0.0171 |
| 9 | 0.1355 | 1.0000 | 3.23 | -0.010 | 22.375 | 0.0692 |
| 10 | 0.0658 | 1.0000 | 1.56 | -0.014 | 10.872 | 0.0987 |

SLOPES             0.690602E 01        0.690602E 01
RMS ERRORS         0.622942E-02        0.430211E-01

DATA REDUCTION FOR BALANCE CALIBRATION WITH HELIUM
MARCH 20, 1970

DENSITY BALANCE CALIBRATION
GAS MOLE WT =  4.003  SCALE CORR = 0.00

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|----------|--------|---------|---------|----------|----------|
| 1 | 0.5857 | 1.0002 | 14.05 | -0.009 | 96.857 | 0.0625 |
| 2 | 0.5320 | 1.0002 | 12.77 | -0.000 | 87.980 | 0.0039 |
| 3 | 0.4788 | 1.0002 | 11.50 | 0.007 | 79.178 | -0.0492 |
| 4 | 0.4254 | 1.0002 | 10.22 | 0.010 | 70.333 | -0.0752 |
| 5 | 0.3658 | 1.0001 | 8.78 | 0.001 | 60.481 | -0.0072 |
| 6 | 0.3181 | 1.0001 | 7.63 | -0.003 | 52.588 | 0.0231 |
| 7 | 0.2660 | 1.0001 | 6.38 | -0.002 | 43.972 | 0.0184 |
| 8 | 0.2126 | 1.0001 | 5.10 | -0.002 | 35.155 | 0.0195 |
| 9 | 0.1589 | 1.0000 | 3.81 | -0.004 | 26.276 | 0.0283 |
| 10 | 0.1061 | 1.0000 | 2.55 | 0.003 | 17.541 | -0.0262 |
| 11 | 0.0553 | 1.0000 | 1.33 | 0.002 | 9.148 | -0.0144 |

SLOPES             0.688934E 01        0.688934E 01
RMS ERRORS         0.536449E-02        0.369575E-01

TABLE G-2.   DENSITY BALANCE CALIBRATIONS USING METHANE

DATA REDUCTION FOR BALANCE CALIBRATION WITH METHANE
MAY 8, 1970

DENSITY BALANCE CALIBRATION
GAS MOLE WT = 16.042   SCALE CORR = 0.15

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|----------|--------|---------|---------|---------|---------|
| 1 | 0.1558 | 0.9997 | 14.95 | 0.003 | 103.311 | -0.0272 |
| 2 | 0.1394 | 0.9997 | 13.36 | -0.002 | 92.366 | 0.0185 |
| 3 | 0.1127 | 0.9998 | 10.80 | -0.000 | 74.654 | 0.0012 |
| 4 | 0.0878 | 0.9998 | 8.41 | -0.002 | 58.147 | 0.0152 |
| 5 | 0.0737 | 0.9998 | 7.07 | 0.004 | 48.836 | -0.0332 |
| 6 | 0.0583 | 0.9998 | 5.59 | 0.000 | 38.634 | -0.0055 |
| 7 | 0.0424 | 0.9999 | 4.06 | -0.007 | 28.118 | 0.0544 |
| 8 | 0.0299 | 0.9999 | 2.86 | -0.002 | 19.786 | 0.0170 |
| 9 | 0.0223 | 0.9999 | 2.12 | -0.019 | 14.791 | 0.1372 |

SLOPES           0.691231E 01        0.691231E 01
RMS ERRORS       0.759720E-02        0.522393E-01


DATA REDUCTION FOR BALANCE CALIBRATION WITH METHANE
MAY 8, 1970

DENSITY BALANCE CALIBRATION
GAS MOLE WT = 16.042   SCALE CORR = 0.15

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|----------|--------|---------|---------|---------|---------|
| 1 | 0.1543 | 0.9997 | 14.76 | -0.002 | 102.023 | 0.0180 |
| 2 | 0.1383 | 0.9997 | 13.24 | 0.012 | 91.413 | -0.0873 |
| 3 | 0.1252 | 0.9997 | 11.97 | -0.003 | 82.745 | 0.0215 |
| 4 | 0.1143 | 0.9997 | 10.93 | 0.001 | 75.526 | -0.0095 |
| 5 | 0.1020 | 0.9998 | 9.75 | -0.006 | 67.427 | 0.0455 |
| 6 | 0.0881 | 0.9998 | 8.42 | -0.001 | 58.201 | 0.0114 |
| 7 | 0.0790 | 0.9998 | 7.55 | -0.006 | 52.224 | 0.0471 |
| 8 | 0.0624 | 0.9998 | 5.97 | 0.004 | 41.225 | -0.0326 |
| 9 | 0.0509 | 0.9999 | 4.87 | 0.003 | 33.634 | -0.0214 |
| 10 | 0.0413 | 0.9999 | 3.95 | -0.002 | 27.313 | 0.0156 |
| 11 | 0.0337 | 0.9999 | 3.21 | -0.009 | 22.248 | 0.0645 |
| 12 | 0.0222 | 0.9999 | 2.12 | -0.009 | 14.717 | 0.0659 |

SLOPES           0.691092E 01        0.691092E 01
RMS ERRORS       0.636635E-02        0.439988E-01

# TABLE G-3.  DENSITY BALANCE CALIBRATIONS USING NITROGEN

DATA REDUCTION FOR BALANCE CALIBRATION WITH NITROGEN
MAY 7, 1970

DENSITY BALANCE CALIBRATION
GAS MOLE WT = 28.016  SCALE CORR = 0.15

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|---------|--------|---------|--------|---------|---------|
| 1  | 0.0825 | 0.9999 | 13.63 | 0.003 | 94.846 | -0.0264 |
| 2  | 0.0731 | 0.9999 | 12.09 | 0.011 | 84.073 | -0.0801 |
| 3  | 0.0689 | 0.9999 | 11.37 | -0.004 | 79.176 | 0.0346 |
| 4  | 0.0626 | 0.9999 | 10.34 | 0.004 | 71.944 | -0.0281 |
| 5  | 0.0567 | 0.9999 | 9.38 | 0.010 | 65.216 | -0.0737 |
| 6  | 0.0483 | 0.9999 | 7.97 | -0.014 | 55.577 | 0.1011 |
| 7  | 0.0390 | 0.9999 | 6.43 | -0.018 | 44.883 | 0.1267 |
| 8  | 0.0320 | 0.9999 | 5.29 | -0.000 | 36.825 | 0.0034 |
| 9  | 0.0288 | 0.9999 | 4.74 | -0.020 | 33.134 | 0.1410 |
| 10 | 0.0232 | 0.9999 | 3.33 | -0.010 | 26.733 | 0.0746 |

| SLOPES | 0.696063E 01 | 0.696062E 01 |
|--------|--------------|--------------|
| RMS ERRORS | 0.117102E-01 | 0.815186E-01 |

DATA REDUCTION FOR BALANCE CALIBRATION WITH NITROGEN
JUNE 19, 1970

DENSITY BALANCE CALIBRATION
GAS MOLE WT = 28.016  SCALE CORR = 0.15

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|---------|--------|---------|--------|---------|---------|
| 1  | 0.0866 | 0.9999 | 14.33 | 0.000 | 99.976 | -0.0065 |
| 2  | 0.0802 | 0.9999 | 13.27 | -0.006 | 92.634 | 0.0479 |
| 3  | 0.0731 | 0.9999 | 12.12 | 0.014 | 84.459 | -0.1034 |
| 4  | 0.0660 | 0.9999 | 10.93 | 0.010 | 76.184 | -0.0756 |
| 5  | 0.0583 | 0.9999 | 9.64 | -0.010 | 67.331 | 0.0720 |
| 6  | 0.0538 | 0.9999 | 8.88 | -0.022 | 62.111 | 0.1545 |
| 7  | 0.0491 | 0.9999 | 8.14 | 0.018 | 56.664 | -0.1295 |
| 8  | 0.0438 | 0.9999 | 7.24 | -0.013 | 50.611 | 0.0967 |

| SLOPES | 0.697716E 01 | 0.697715E 01 |
|--------|--------------|--------------|
| RMS ERRORS | 0.137813E-01 | 0.961571E-01 |

TABLE G-4.  DENSITY BALANCE CALIBRATION USING UHP METHANE
           AND UHP CARBON DIOXIDE

DATA REDUCTION FOR BALANCE CALIBRATION WITH UHP C1
JULY 2, 1970

DENSITY BALANCE CALIBRATION
GAS MOLE WT = 16.042   SCALE CORR = 0.25

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|---------|--------|--------|--------|--------|--------|
| 1 | 0.1468 | 0.9997 | 13.91 | -0.004 | 97.036 | 0.0321 |
| 2 | 0.1340 | 0.9997 | 12.71 | 0.009 | 88.567 | -0.0689 |
| 3 | 0.1284 | 0.9997 | 12.17 | 0.005 | 84.833 | -0.0369 |
| 4 | 0.1188 | 0.9997 | 11.26 | 0.004 | 78.492 | -0.0315 |
| 5 | 0.1122 | 0.9998 | 10.62 | -0.006 | 74.108 | 0.0471 |
| 6 | 0.1041 | 0.9998 | 9.85 | -0.011 | 68.773 | 0.0825 |
| 7 | 0.0966 | 0.9998 | 9.15 | -0.002 | 63.826 | 0.0166 |
| 8 | 0.0885 | 0.9998 | 8.38 | -0.001 | 58.447 | 0.0075 |
| 9 | 0.0820 | 0.9998 | 7.77 | 0.005 | 54.149 | -0.0364 |
| 10 | 0.0739 | 0.9998 | 7.01 | 0.009 | 48.821 | -0.0646 |
| 11 | 0.0678 | 0.9998 | 6.42 | -0.002 | 44.790 | 0.0195 |
| 12 | 0.0604 | 0.9998 | 5.71 | -0.011 | 39.897 | 0.0771 |

SLOPES          0.697373E 01      0.697372E 01
RMS ERRORS      0.709188E-02      0.494576E-01

DATA REDUCTION FOR BALANCE CALIBRATION WITH UHP CO2
JULY 16, 1970

DENSITY BALANCE CALIBRATION
GAS MOLE WT = 44.010   SCALE CORR = 0.50

| PT | PRESSURE ATM | Z FACTOR | CURRENT MA | CURRENT DIFF | DENSITY GM/M**3 | DENSITY DIFF |
|----|---------|--------|--------|--------|--------|--------|
| 1 | 0.0567 | 0.9997 | 14.70 | -0.009 | 102.680 | 0.0693 |
| 2 | 0.0546 | 0.9997 | 14.19 | 0.007 | 98.998 | -0.0526 |
| 3 | 0.0506 | 0.9997 | 13.12 | -0.006 | 91.627 | 0.0449 |
| 4 | 0.0484 | 0.9997 | 12.57 | 0.006 | 87.700 | -0.0427 |
| 5 | 0.0456 | 0.9997 | 11.84 | 0.008 | 82.590 | -0.0570 |
| 6 | 0.0422 | 0.9997 | 10.94 | -0.002 | 76.384 | 0.0196 |
| 7 | 0.0392 | 0.9998 | 10.17 | 0.006 | 70.941 | -0.0485 |
| 8 | 0.0346 | 0.9998 | 8.98 | -0.009 | 62.752 | 0.0689 |

SLOPES          0.698035E 01      0.698035E 01
RMS ERRORS      0.754382E-02      0.526585E-01

required molecular weight.  Using similar reasoning, the results of Table G-2 indicate that the CP grade methane used had a true molecular weight of approximately 16.2.  The calibration slopes for nitrogen given in Table G-3 are close to the accepted value of 6.98.  This might have been expected since the molecular weights of any impurities are likely to be close to that of nitrogen.

## G.3  Density Balance Data Reduction Program

A listing of the FORTRAN program used to calculate the composition of binary mixtures and to calibrate the density balance is reproduced on pages G-8 to G-10.  Comment cards are used to assist the user.  The program calls one subroutine called ZB.  This subroutine calculates the compressibility factor for the various gases using simple approximations for second virial coefficients.

```
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C    THIS PROGRAM IS USED TO CALCULATE THE COMPOSITIONS OF        *
C    BINARY MIXTURES FROM DENSITY BALANCE MEASUREMENTS.  THE      *
C    PROGAM CAN ALSO BE USED FOR DENSITY BALANCE CALIBRATION.     *
C    THE FOLLOWING CODE IS USED TO DESIGNATE THE GAS(ES)          *
C        KEY = 1, CALIBRATE DENSITY BALANCE WITH HELIUM           *
C        KEY = 2, CALIBRATE DENSITY BALANCE WITH METHANE          *
C        KEY = 3, CALIBRATE DENSITY BALANCE WITH NITROGEN         *
C        KEY = 4, CALIBRATE DENSITY BALANCE WITH BUTANE           *
C        KEY = 5, CALIBRATE DENSITY BALANCE WITH CO2              *
C        KEY = 6, ANALYSIS BY DENSITY BALANCE, METHANE-BUTANE     *
C        KEY = 7, ANALYSIS BY DENSITY BALANCE, METHANE-PENTANE    *
C        KEY = 8, ANALYSIS BY DENSITY BALANCE, METHANE-HEXANE     *
C        KEY = 9, ANALYSIS BY DENSITY BALANCE, METHANE-CO2        *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      REAL  TB(20), ATM(20), W(20), XL(20), XH(20), P(20),
     1 X(20), Y(20), Z(20), DX(20), DY(20)
      INTEGER NAME1(17), NAME2(20), ITEST(20)
      IREAD=5
      IRITE=6
    1 FORMAT(I1,I2,I3,37A2)
    2 FORMAT(5F5.3)
    3 FORMAT('1DATA REDUCTION FOR ',17A2/1X,20A2/'0DENSITY '
     1'BALANCE CALIBRATION'/' GAS MOLE WT =',F7.3,
     2'   SCALE CORR =',F5.2,/'0PT  PRESSURE     Z      CURRENT'
     3'  CURRENT  DENSITY  DENSITY'/7X,'ATM      FACTOR     MA'
     4'        DIFF    GM/M**3   DIFF'/' --  --------- -------'
     5'  --------- --------- -------- --------'/)
    4 FORMAT('1DATA REDUCTION FOR ',17A2/1X,20A2/'0DENSITY '
     1'BALANCE ANALYSES, RUN',I3,/' LIGHT MOLE WT =',F7.3,15X,
     2'SLOPE =',F6.3,/' HEAVY MOLE WT =',F7.3,15X,'SCALE COR'
     3' =',F5.2/'0NO  SYSTEM    SAMPLE      Z     CURRENT  MOL'
     4'E FR  MOLE FR'/6X,'PSIA      ATM     FACTOR     MA    '
     5'  ET-ANE   HEAVY'/' --  ------   -------   --------',4(5H ------ )/)
    6 FORMAT(I1,2I2,F5.0,6F5.2,3F5.0)
    7 FORMAT(1X,I2,2F9.4,F8.2,F10.3,F9.3,F9.4)
    8 FORMAT('0SLOPES',9X,E13.6,5X,E13.6,/
     1'  RMS ERRORS',5X,F13.6,5X,F13.6)
    9 FORMAT(1X,I2,F9.0,2F9.4,F8.2,F10.4,F9.4)
   11 FORMAT(37X,F10.4,F9.4)
   14 FORMAT(1H )
   20 READ(IREAD,1)LABEL,N,IRUN,NAME1,NAME2
      GO TO (30,40,50,200),LABEL
   30 READ(IREAD,2)WC,W1,W2,SCALE,SLOPE
      WRITE(IRITE,3)NAME1,NAME2,WC,SCALE
      GO TO 50
   40 READ(IREAD,2)WC,W1,W2,SCALE,SLOPE
      WRITE(IRITE,4)NAME1,NAME2,IRUN,W1,SLOPE,W2,SCALE
   50 LAP=0
      DO 60 I=1,N
      XL(I)=1.0
      READ(IREAD,6)KEY,IRUN,ITEST(I),P(I),HL,HR,TM,X(I),TB(I)
C     CORRECTION OF MANOMETER READINGS TO ZERO DEG. C.
      HT=(HL+HR+SCALE)*(1.0-(163.4E-06*TM)/(1.0+181.8E-06*TM))
```

```fortran
      ATM(I)=HT*1.0005/760.0
   60 CONTINUE
      SUMX=0.0
      IF(LABEL-3)70,140,70
   70 DO 100 I=1,N
      TA=TB(I)+273.16
      AAA=ATM(I)
      XX=XL(I)
      CALL ZB(KEY,TA,AAA,XX,Z(I))
      IF(KEY-3)90,80,80
   80 X(I)=SLOPE*X(I)*Z(I)**2.*18E-06*TA/ATM(I)
      XL(I)=(XX-XL(I))/(XX2-1)
      XH(I)=1.0-XL(I)
      SUMX=SUMX+XL(I)
      GO TO 100
   90 Y(I)=ATM(I)*WC/(Z(I)*92.054E-06*TA)
  100 CONTINUE
      IF(KEY-3)110,120,120
  110 SXX=0.0
      SXY=0.0
      SYY=0.0
C     CALIBATION POINTS ARE WEIGHTED BY SQRT(DENSITY)
      DO 111 I=1,N
      SXX=SXX+X(I)*X(I)*SQRT(Y(I))
      SXY=SXY+X(I)*Y(I)*SQRT(Y(I))
      SYY=SYY+Y(I)*Y(I)*SQRT(Y(I))
  111 CONTINUE
      BX=SYY/SXY
      BY=SXY/SXX
      SDX=0.0
      SDY=0.0
      DO 112 I=1,N
      DX(I)=X(I)-Y(I)/BX
      DY(I)=Y(I)-BY*X(I)
      SDX=SDX+DX(I)*DX(I)
      SDY=SDY+DY(I)*DY(I)
  112 CONTINUE
      SDX=SQRT(SDX/N)
      SDY=SQRT(SDY/N)
      WRITE(IRITE,7)(I,ATM(I),Z(I),X(I),DX(I),Y(I),DY(I),I=1,N)
      WRITE(IRITE,8)BX,BY,SDX,SDY
      GO TO 10
  120 LAP=LAP+1
      IF(LAP-1)130,60,130
  130 WRITE(IRITE,9)(ITEST(I),P(I),ATM(I),Z(I),X(I),XL(I),
     1XH(I),I=1,N)
      IF(N-1)131,132,131
  131 XX=SUMX/FLOAT(N)
      XIX=1.0-XX
      WRITE(IRITE,11)XX,XIX
  132 WRITE(IRITE,14)
      GO TO 20
  140 LAP=LAP+1
      GO TO 20
  200 CALL EXIT
      END
```

```
      SUBROUTINE ZB(KEY,TA,ATM,X,Z)
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C  THIS SUBROUTINE CALCULATES THE COMPRESSIBILITY FACTOR     *
C  FOR THE PARTICULAR GAS SPECIFIED BY 'KEY' USING SECOND     *
C  VIRIAL COEFFICIENT DATA WHICH APPLY AT ROOM TEMPERATURE    *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      R=ATM/(82.054*TA)
      GO TO(10,20,30,40,50,60,70,80,90),KEY
   10 Z=1.0+12.0*R
      RETURN
   20 Z=1.0+(42.441-16711.3/TA-2501485.5/(TA*TA))*R
      RETURN
   30 Z=1.0-(8.6+0.191111*(TA-318.16))*R
      RETURN
   40 Z=1.0+255.0*(0.43-0.866*425.2/TA-0.694*(425.2/TA)**2
     1-0.1125*(425.2/TA)**4.5)*R
      RETURN
   50 Z=1.0+(0.9*TA-389.7)*R
      RETURN
   60 E=244.0-1.6*(TA-273.16)
      B22=255.0*(0.43-0.866*425.2/TA-0.694*(425.2/TA)**2
     1-0.1125*(425.2/TA)**4.5)
      GO TO 100
   70 E=474.0-3.0*(TA-273.16)
      B22=311.0*(0.43-0.866*469.6/TA-0.694*(469.6/TA)**2
     1-0.15*(469.8/TA)**4.5)
      GO TO 100
   80 E=483.0-6.52*(TA-273.16)
      B22=368.0*(0.43-0.586*507.9/TA-0.694*(507.9/TA)**2
     1-0.1175*(507.9/TA)**4.5)
      GO TO 100
   90 E=26.0-0.32*(TA-273.16)
      B22=0.9*TA-389.7
  100 B11=42.441-16711.3/TA-2501485.5/(TA*TA)
      B12=E+0.5*(B11+B22)
      XI=1.0-X
      B=X*X*B11+2.0*X*XI*B12+XI*XI*B22
      Z=1.0+B*R
      RETURN
      END
```

APPENDIX H

INSTRUMENT CALIBRATION DATA

## TABLE H-1.   PRESSURE GAUGE CALIBRATIONS

| Serial No. | H26191 | H19154R | H39687 | H39217 | H39217 |
|---|---|---|---|---|---|
| CPE No. | 1371 | 1390 | 1060 | 1344 | 1344 |
| Range | 0-1500 | 0-1500 | 0-5000 | 0-5000 | 0-5000 |
| Date | Jan. 6/69 | Jan. 6/69 | Jan. 15/69 | Jan. 15/69 | June 4/69 |
| DWG, psig | psig | psig | psig | psig | psig |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 200 | 200 | 200 | | | |
| 250 | | | 250 | 250 | |
| 400 | 400 | 400 | | | |
| 500 | | | 500 | 500 | 500 |
| 600 | 600 | 600 | | | |
| 750 | | | 750 | 750 | |
| 800 | 800 | 800 | | | |
| 1000 | 1000 | 1000 | 1005 | 1000 | 1000 |
| 1200 | 1200 | 1200 | | | |
| 1250 | | | 1250 | 1250 | |
| 1400 | 1400 | 1400 | | | |
| 1500 | 1500 | 1500 | 1500 | 1500 | 1500 |
| 1750 | | | 1750 | 1750 | |
| 2000 | | | 2000 | 2005 | 2000 |
| 2250 | | | 2250 | 2250 | |
| 2500 | | | 2500 | 2500 | 2500 |
| 2750 | | | 2756 | 2750 | |
| 3000 | | | 3000 | 3000 | 3000 |
| 3250 | | | 3250 | 3250 | |
| 3500 | | | 3505 | 3500 | 3500 |
| 3750 | | | 3755 | 3750 | |
| 4000 | | | 4000 | 4000 | 4000 |
| 4250 | | | 4250 | 4250 | |
| 4500 | | | 4505 | 4500 | 4500 |
| 4750 | | | 4750 | 4750 | |
| 5000 | | | 5000 | 5000 | 5000 |

Note:   The Ruska dead weight gauge in the Department of
        Chemical and Petroleum Engineering Standards Laboratory
        was used in all calibrations.

        Errors smaller than 0.1 per cent of full scale reading
        were not recorded.

TABLE H-2.   THERMOCOUPLE CALIBRATION

| Serial No. | #1 (Cell II) | | #4 (Cell I) | | #3 (Cell III) | |
|---|---|---|---|---|---|---|
| Type | Fe-constantan | | Fe-constantan | | Fe-constantan | |
| Date | May 8, 1970 | | May 8, 1970 | | May 8, 1970 | |
| Water Bath | emf, millivolts | | emf, millivolts | | emf, millivolts | |
| Temp. °F | Ref. J. | TC | Ref. J. | TC | Ref. J. | TC |
| 100 | 1.951 | 1.956 | 1.951 | 1.956 | 1.951 | 1.956 |
| 130 | 2.821 | 2.827 | 2.821 | 2.826 | 2.821 | 2.826 |
| 160 | 3.700 | 3.705 | 3.706 | 3.712 | 3.704 | 3.711 |
| 190 | 4.607 | 4.612 | 4.607 | 4.612 | 4.605 | 4.612 |

Note:   Ref. J. refers to the emf measured with respect to the reference junction used on the equipment.

TC refers to the emf measured at the thermocouple.

All voltages were measured with a Leeds-Northrup Model K-3 potentiometer.

APPENDIX I

PHOTOGRAPHS OF RETROGRADE LIQUID CAPILLARY STRUCTURES
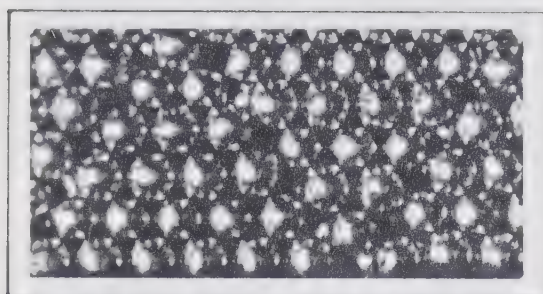
1500 PSIA
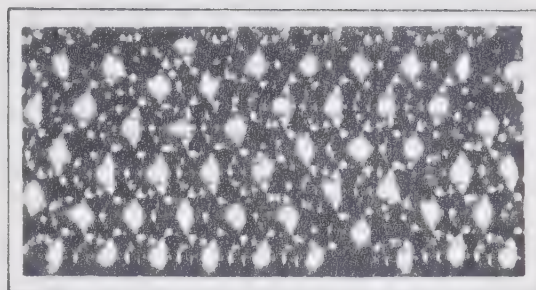


800 PSIA
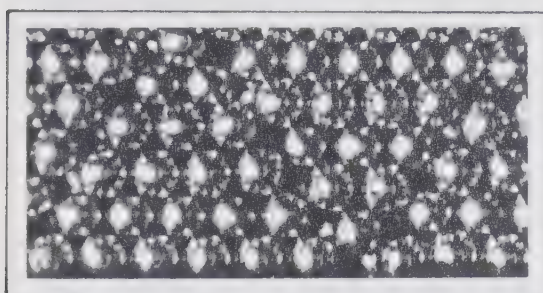


1250 PSIA
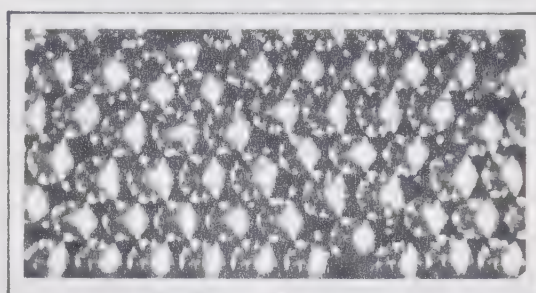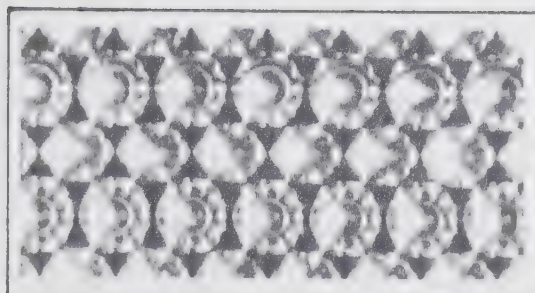


600 PSIA
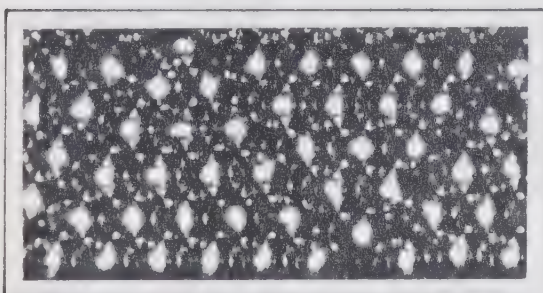


1000 PSIA
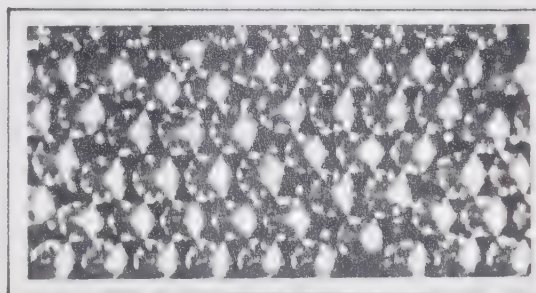


400 PSIA
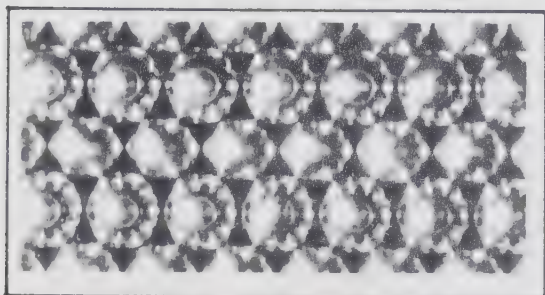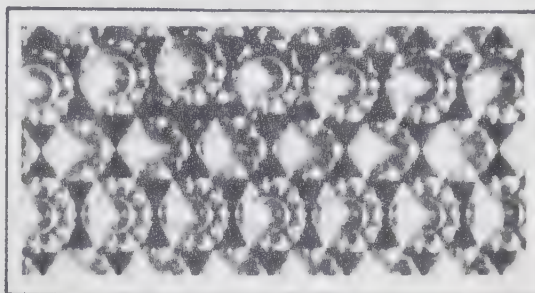
Figure I-1.  Photographs of Liquid Capillary Structures Formed
            During Pressure Depletion of the Methane-n-Butane
            Mixture in Run 4.
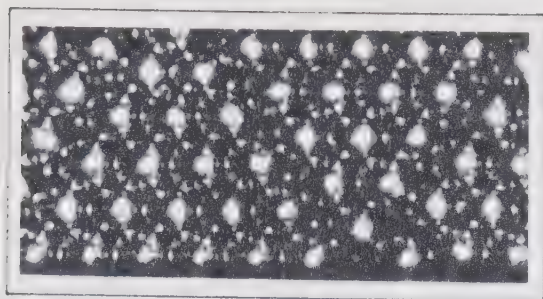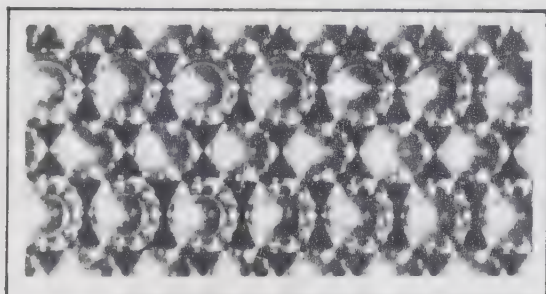
2000 PSIA
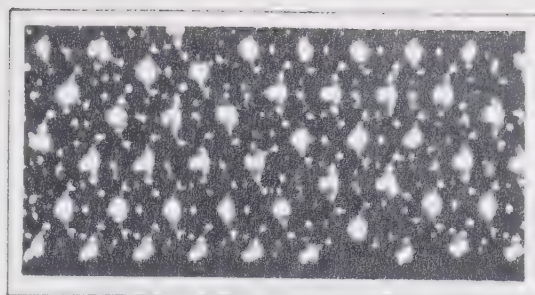
800 PSIA
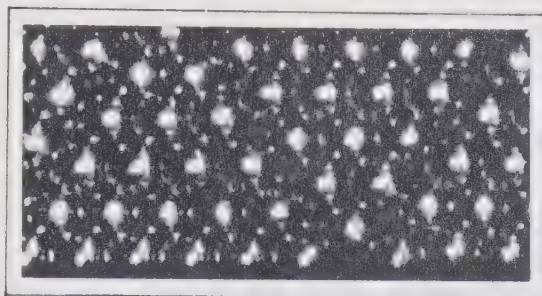
1500 PSIA
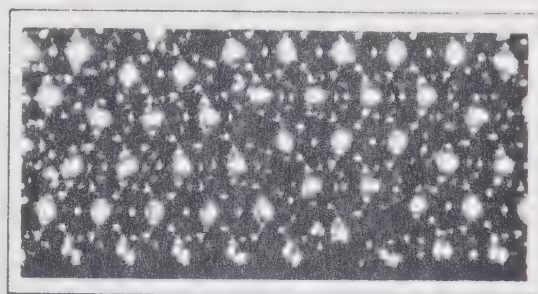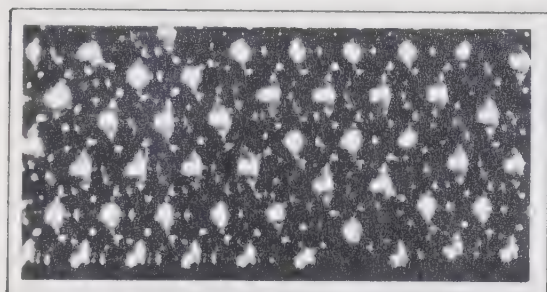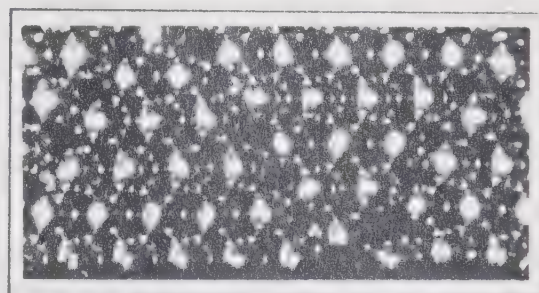
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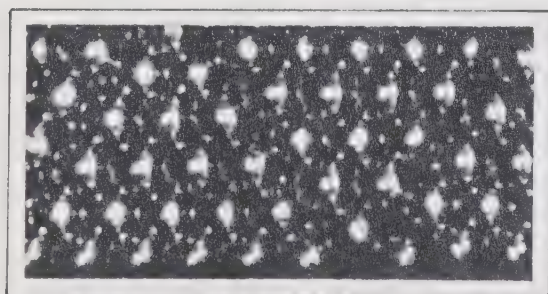
1250 PSIA
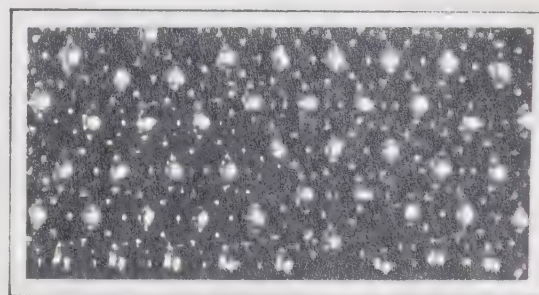
400 PSIA

1000 PSIA

200 PSIA

Figure I-2.  Photographs of Liquid Capillary Structures Formed
During Pressure Depletion of the Methane-n-Butane
Mixture in Run 5.
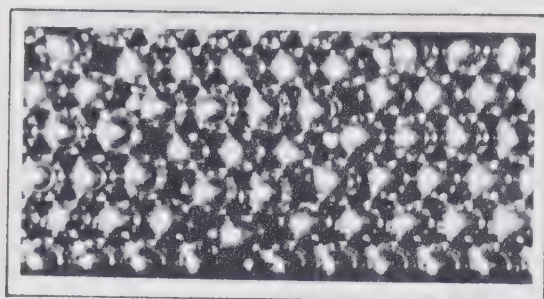
1500 PSIA
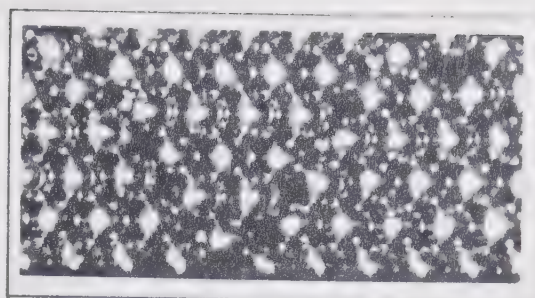
600 PSIA
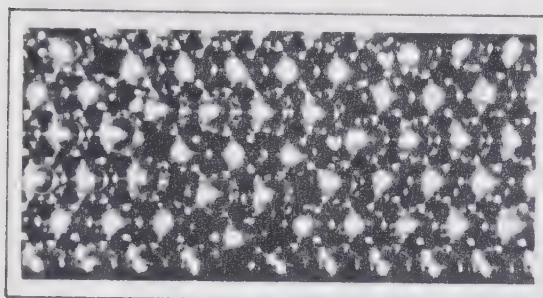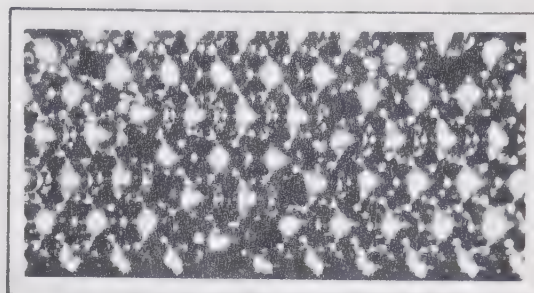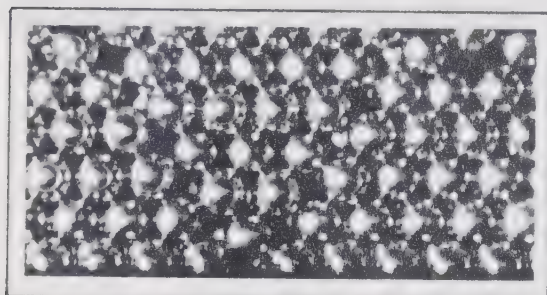
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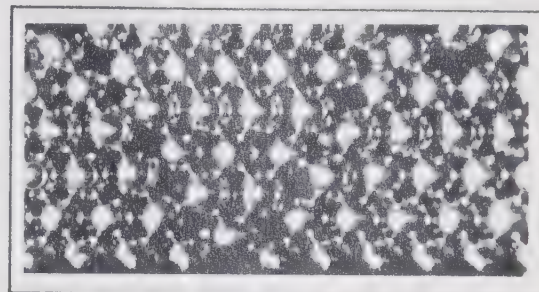
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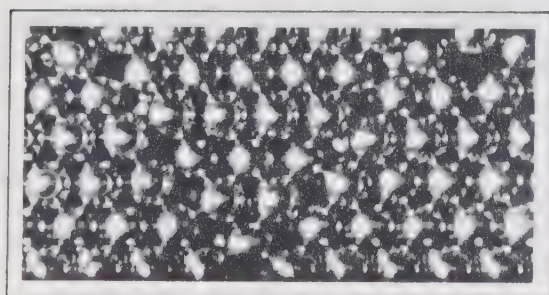
1000 PSIA

200 PSIA

800 PSIA
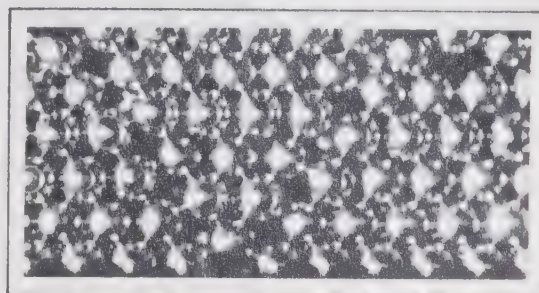
100 PSIA

Figure I-3.  Photographs of Liquid Capillary Structures Formed
During Pressure Depletion of the Methane-n-Hexane
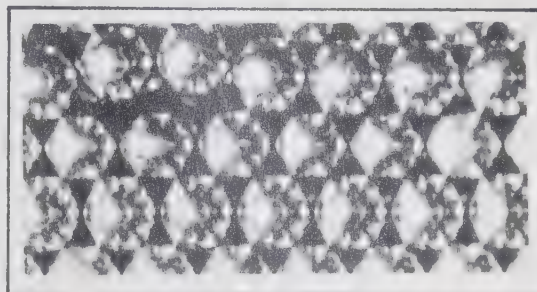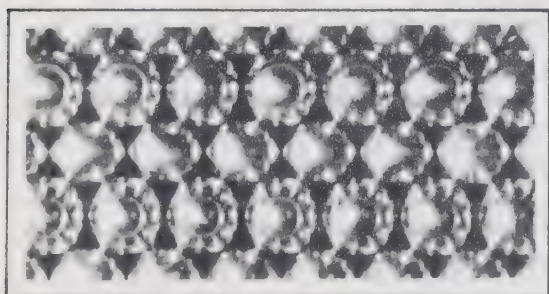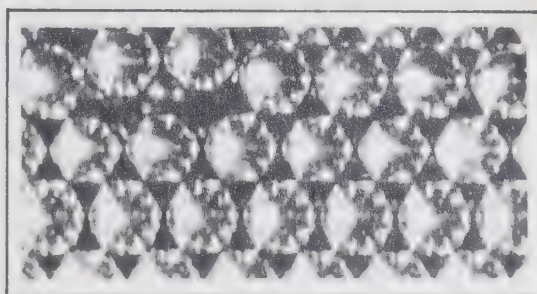Mixture in Run 7.
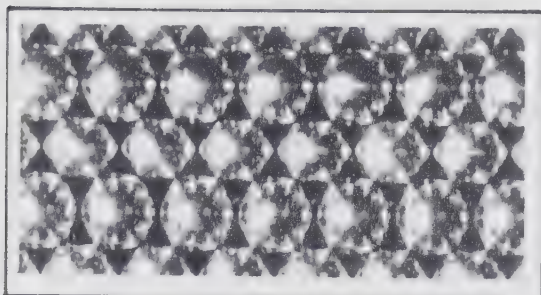
1750 PSIA

800 PSIA

1500 PSIA

600 PSIA

1250 PSIA

400 PSIA

1000 PSIA

300 PSIA

Figure I-4. Photographs of Liquid Capillary Structures Formed During Pressure Depletion of the Methane-n-Butane Mixture in Run 13.

B30043